

The Institution of Gas Engineers

GAS WORKS EFFLUENTS AND AMMONIA

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GAS WORKS EFFLUENTS AND AMMONIA

I PREFACE

On 13th April, 1926, at a meeting of the Central Executive Board of the National Gas Council, reference was made to a communication which had been received from the Halifax Corporation Gas Department, calling attention to the serious difficulty of the disposal of gas works liquor effluent and suggesting an investigation of the problem, and also to a discussion of the subject between Dr. T. Lewis Bailey, Chief Inspector under the Alkali (etc.) Act, the British Sulphate of Ammonia Federation and the National Gas Council.

Mr. Charles F. Botley, President of The Institution of Gas Engineers at the time, pointed out that the subject was essentially one for research, and the matter was therefore referred to the Institution. With the approval of the Council of the Institution, a Liquor Effluents Research Committee (later called the Liquor Effluents Sub-Committee) was constituted on 8th June, 1926.

For a time, Reports were made to the Central Executive Board of the National Gas Council, which provided the necessary financial help, but in 1928 the work was incorporated as part of the research programme of The Institution of Gas Engineers. The amount expended to such date, including a contribution of £105 from the British Sulphate of Ammonia Federation, was £959. From 1928 onwards the cost of the work, with the exception of a further contribution of £100 from the British Sulphate of Ammonia Federation and of £150 from the National Gas Council, has been met from the Special Purposes Fund of the Institution.

The work in connexion with liquor effluents could not be considered without reference to ammonia, regarding which critical questions arose. It was therefore decided in 1928 by the Council of the Institution to constitute an Ammonia Sub-Committee which worked in conjunction with the Liquor Effluents Sub-Committee until 1930, when the two Sub-Committees were combined in the Liquor Effluents and Ammonia Sub-Committee, which in 1934 became the Liquor Effluents and Ammonia Committee. Five Reports were presented by the Liquor Effluents Sub-Committee, three by the Ammonia Sub-Committee, and seven have been presented so far by the Liquor Effluents and Ammonia Committee.

The membership of the original Liquor Effluents Research Committee comprised:

Mr. Charles F. Botley (*Chairman*); Dr. T. Lewis Bailey; Dr. H. T. Calvert; Mr. P. N. Langford; Mr. F. Lee; Mr. W. E. Price; Dr. E. W. Smith; Professor Arthur Smithells; Mr.

John Wilkinson; Professor John W. Cobb (*Honorary Secretary*); Dr. A. Parker (*Deputy Secretary*).

The membership of the original Ammonia Sub-Committee comprised:

Mr. Charles F. Botley (*Chairman*); Mr. H. E. Bloor; Mr. E. V. Evans; Mr. H. Hollings; Mr. P. G. G. Moon; Dr. A. Parker; Mr. T. F. E. Rhead; Dr. E. W. Smith; Mr. W. W. Townsend; Mr. John Wilkinson; Professor John W. Cobb (*Honorary Secretary*).

In addition, the following have also served on these two Committees or on the Liquor Effluents and Ammonia Committee:

Mr. W. A. Damon, Mr. J. W. McLusky, Mr. P. Parrish.

Dr. A. Parker (1926 to 1929), Dr. A. C. Monkhouse (1926 to 1931), and Dr. Arthur Key (1931 to 1937), assisted by Mr. W. Etheridge (1930 to 1937), and Dr. A. H. Eastwood (1933 to 1936), have been responsible for carrying out the research programme of these Committees.

Through the courtesy of the various authorities and officials concerned and the facilities granted by them without charge to the Committees, the latter have been enabled to make investigations at the Gas Works at Hinckley and Coventry and at the Sewage Works at Hinckley and Leamington. Some of the laboratory work has been done, with the collaboration of the Livesey Professor, in the Department of Coal Gas and Fuel Industries at the University of Leeds, where also facilities have been freely provided.

The recorded expenditure in connexion with the work of the above-mentioned Committees from 1928 to 1937 (both inclusive) was £12,785. This is distinct from the many contributions in time and facilities already referred to and from the considerable sums expended by individual Gas Undertakings in investigations relating to liquor effluents and ammonia.

The Liquor Effluents and Ammonia Committee feels that a summary of the results of the investigations of the Committees and a comprehensive survey of the present state of knowledge of the whole subject should now be published. These are given in the following review "Gas Works Effluents and Ammonia," which is presented in the confident hope that the information it contains will be of permanent value to members of The Institution of Gas Engineers and others interested in the subject or confronted with problems arising in connexion therewith.

II GAS WORKS AMMONIACAL LIQUOR, ITS NATURE AND COMPOSITION

In the carbonization of coal for the production of town gas there are four main classes of products; gas, coke, tar and an aqueous product, ammoniacal liquor. It is with the nature, treatment and ultimate disposal of this aqueous product that this book is principally concerned.

During carbonization a considerable part of the mass of the coal leaves the retort in the gaseous phase. The gases pass through the foul gas main, where a certain amount of condensation occurs with the deposition of tar and usually some liquor, to the condensers, where cooling is completed. Being now relatively free from tar and moisture, the gases are treated for the removal of the residual ammonia, after which they are subjected to purification by oxide of iron. The ammonia, together with a proportion of the hydrogen sulphide and smaller quantities of other substances, is removed in washers or scrubbers, where the gas is brought into intimate contact with an aqueous liquid containing very little or no ammonia. This liquid may be either water or a very weak ammonia solution previously condensed from the gas.

NOMENCLATURE

The aqueous products of coal carbonization are called liquors and it will be seen that, according to the preceding paragraph, liquors are produced at three chief points in the system:

- (1) In the foul gas main and before the condensing system, this condensate usually being called the retort house liquor;
- (2) In the condensers themselves, the condenser liquor;
- (3) In scrubbing the gas free from ammonia, the scrubber or washer liquor.

The mixture of liquors from the first two sources is often called virgin liquor, and to the whole of the liquors combined are given the names crude liquor, raw liquor or ammoniacal liquor. To avoid confusion the term "ammoniacal liquor" will be used throughout this book.

NATURE OF AMMONIACAL LIQUOR

As signified by its name the most important constituent of ammoniacal liquor is ammonia. This is not usually present as such, but the larger part occurs as salts, chiefly sulphides, carbonates and cyanides, from which the ammonia is liberated by boiling. The ammonia present as such salts is called "free" ammonia. The remainder, called the "fixed" ammonia, occurs as salts, mainly chloride, thiocyanate and thio-

sulphate, from which it can only be liberated by boiling after the addition of an alkali.

Ammoniacal liquor also contains small quantities of many other substances which are also contained in tar. Of these the most important are the acidic bodies, which are mainly phenolic in character and which are for convenience divided into "phenols" (the monohydric phenols) and "higher tar acids" (polyhydric phenols and other complex acidic bodies). There are also present neutral bodies, including various hydrocarbon oils, naphthalene and benzene.¹ These are comparatively unimportant for the purposes of this book. The same may be said of the basic organic compounds, pyridine and related bodies, which are not therefore considered here in detail.

ANALYSIS OF AMMONIACAL LIQUOR

The methods of analysis of ammoniacal liquor are described in Appendix 1. The results are expressed in most cases as g. per 100 c.c., but higher tar acids are recorded as g. oxygen absorbed per 100,000 c.c. liquor in the burette aeration test.* They could, however, be expressed as catechol in g. per 100 c.c. by dividing by 490. The "Oxygen Absorption" (O/A), the determination of which is described in Appendix 1, is also expressed as g. oxygen absorbed per 100,000 c.c.; the significance of this test will become apparent later when the influence of gas liquors on sewage is studied (p. 37).

The strength of ammoniacal liquor is also commonly expressed as "Ounce Strength" and occasionally as "degrees Twaddell". Ounce Strength indicates the number of ounces of pure sulphuric acid which would neutralize the ammonia contained in a gallon of liquor. It can be obtained from the ammonia content expressed as g. per 100 c.c. by multiplying by 4.61. Degrees Twaddell refers to a scale for measuring densities and is 200 times the amount by which the density exceeds unity. One degree Twaddell is sometimes regarded as being equivalent to two-ounce strength, but this relationship is by no means accurate, since other constituents of the liquor influence the density more than does the ammonia.

RELATIVE COMPOSITIONS OF AMMONIACAL LIQUORS FROM DIFFERENT PARTS OF THE PLANT

The composition of ammoniacal liquor depends on the nature and moisture content of the coal carbonized, the system of carbonization employed, the type of condensing and scrubbing system, and the way in which the last two are worked. There is, however, a general relationship irrespec-

* The liquor, made alkaline with caustic soda, is shaken with a known volume of air, and the amount of oxygen taken up is measured (see Appendix 1, p. 134).

tive of other factors, between the retort house liquor, the condenser liquor, and the scrubber liquor. This relationship is indicated in Table 1, giving results obtained in testing an installation of intermittent vertical chambers.²

The gases leaving the retorts contain almost all the components of tar and liquor. In the retort house much of the tar separates, but the temperature of the gas is too high for much liquor to condense. The presence of liquor in this part of the plant is due largely to the fact that often it is circulated through the gas mains to assist in tar separation and to ensure uninterrupted working. This liquor becomes highly con-

TABLE 1.—*Analysis of Ammoniacal Liquor from different parts of the Plant*

Description of Liquor.	Retort House Liquor.	Condenser Liquor.	Scrubber Liquor.
1	2	3	4
g. per 100 c.c.			
Density, ° Tw... ..	4.5	4.0	8.0
Composition:			
Free ammonia	0.41	2.10	3.81
Fixed ammonia	1.62	0.13	0.08
Sulphides, as H ₂ S	0.02	0.50	0.84
Thiosulphate, as S	0.19	0.03	0.03
Thiocyanate, as CNS	0.31	0.07	0.06
Chloride, as HCl	2.29	0.18	0.26
Carbonate, as CO ₂	Nil	1.92	3.61
Phenol, as C ₆ H ₅ OH	0.35	0.47	0.05
Pts. per 100,000.			
Higher tar acids (O ₂ absorbed in aeration test)	73	11	Nil
Oxygen absorption (4 hr., 27° C.), due to:			
Sulphide.. ..	24	667	1,130
Phenols	619	839	80
Thiosulphate	164	29	27
Thiocyanate	254	55	51
Difference	589	318	285
Total	1,650	1,902	1,573
Oxygen absorption, omitting sulphide	1,626	1,241	443

taminated with the less volatile substances, notably ammonium chloride and higher tar acids, but contains relatively little free ammonia, carbonates and sulphides, as is apparent from Table 1.

In an efficient plant, such as that referred to in connexion with Table 1, tar separation should be almost complete by the time the gas enters the condensers. The condenser liquor consequently contains only small quantities of higher tar acids, which are not volatile in steam and which therefore come down largely with the tar. For the same reason the fixed ammonia and chloride contents are also low. On the

other hand, this liquor is relatively rich in more volatile substances, such as free ammonia, sulphide, carbonates and phenols.

The scrubber liquor is free from higher tar acids and contains little chloride or fixed ammonia. It contains very little phenol, since this is largely removed from the gas in the condensers. It is rich, however, in those substances, soluble in water, which are not wholly removed from the gas in the condensers, namely, free ammonia, carbonate and sulphide. Often this liquor contains small quantities of cyanide.

Thiosulphate and thiocyanate do not occur in appreciable quantities in the gas leaving the retorts but are produced subsequently by oxidation of sulphide and cyanide. The extent of this oxidation depends on the amount of oxygen in the gas. Where no oxygen is drawn into the gas at the retort and where air for purification purposes is supplied at the inlet to the purifiers, opportunity for oxidation is small and the thiosulphate and thiocyanate contents of the liquors are also small throughout, as in Table 1. Where air for purification is admitted at the inlet of the exhausters, oxidation will occur in the scrubbers and the concentration of thiosulphate and thiocyanate in the scrubber liquor will increase accordingly. It should be borne in mind that this oxidation of sulphide and cyanide to thiosulphate and thiocyanate converts a corresponding quantity of free ammonia into fixed ammonia and, for this reason, the fixed ammonia content of scrubber liquor is occasionally large.

The oxygen absorption, in parts per 100,000, due to the different constituents of gas works liquors, is calculated from the concentration of these substances in g. per 100 c.c., using the following factors:

O/A due to sulphide	=	sulphide concentration,	as H_2S	x 1345.
" " " thiosulphate	=	thiosulphate concentration,	as S	x 856.
" " " thiocyanate	=	thiocyanate concentration,	as CNS	x 827.
" " " phenols	=	phenol concentration,	as $\text{C}_6\text{H}_5\text{OH}$	x 1780.

When the values attributable to the above substances are subtracted from the total oxygen absorption as determined, there remains a certain amount unaccounted for. This is expressed as a "difference" figure and its existence is due largely to the oxygen absorption of the higher tar acids, which cannot readily be calculated. No doubt it is also due in part to the presence of other substances of which the concentrations are not determined, but in spite of this the difference figure of a mixed gas works liquor usually bears an almost quantitative relationship to the higher tar acid content. This is not always true for liquors from different points from the same Works.

The liquors referred to in Table 1 do not vary much in oxygen absorption. It does not follow from this that they will have an equal effect on sewage or in causing pollution in streams, nor does it follow that the spent gas liquors produced

in the distillation of these ammoniacal liquors little in oxygen absorption. Sulphide, for instance, is removed from spent liquors, and the effect of its removal on oxygen absorption is indicated in Table 1 and other parts of this Section by an additional set of figures.

COMPOSITION OF AMMONIACAL LIQUORS FROM DIFFERENT TYPES OF CARBONIZING SYSTEMS

Liquors obtained from different types of carbonizing systems show marked differences in composition, depending largely on the degree of heat to which the gases liberated

TABLE 2.—*Approximate Average Composition of Ammoniacal Liquor*

Carbonizing System.	Horizontal Retorts.	Continuous Vertical Retorts.
I		
	g. per 100 c.c.	
Composition:		
Ammonia, free	1.50	1.00
Ammonia, fixed	0.50	0.33
Sulphide, as H_2S	0.25	0.15
Cyanide, as H_2CN	0.010	0.005
Thiosulphate, as S	0.10	0.10
Thiocyanate, as CNS	0.20	0.20
Phenols, as C_6H_5OH	0.25	0.35
	Pts. per 100,000.	
Higher tar acids, O_2 absorbed	30	130
Oxygen absorption (4 hr., $27^\circ C.$), due to:		
Sulphide ..	336	200
Phenol ..	445	620
Thiosulphate	85	85
Thiocyanate	165	165
Difference	160	580
Total	1,191	1,650
Oxygen absorption, omitting sulphide	855	1,450

from the coal are subjected. Table 2 gives typical analyses of liquors obtained from carbonization in horizontal and in continuous vertical retorts, these having been selected as the most common types in use in this country. These analyses may be regarded as approximate averages but must not be taken as representing the composition of the ammoniacal liquor produced by any particular Undertaking. Table 3 gives the composition of four actual liquors, specially chosen to illustrate and emphasize this point. It will be seen from these analyses that wide variations exist in the concentration of nearly every constituent, and that large alterations can be brought about by choice of coal and conditions of working.

As illustrating this point the figures in column 1 of Table 3 represent results obtained regularly in the carefully controlled carbonization of Durham coal on a very large scale.

TABLE 3.—*Showing the Wide Variations in Composition of Ammoniacal Liquors from Different Gas Undertakings*

1. Durham coal carbonized in horizontal retorts, the volume of liquor being kept as small as possible.
2. Somerset coal carbonized in horizontal retorts ; no effort made to minimize volume of liquor.
3. Yorkshire coal carbonized in vertical retorts ; excess air in crude gas and long time of contact between gas and liquor in scrubbing system.
4. Yorkshire coal carbonized in vertical retorts ; much better conditions of working than 3.

	1	2	3	4
	g. per 100 c.c.			
Composition :				
Ammonia, free	1.98	1.15	1.03	1.34
Ammonia, fixed	0.40	0.23	1.09	0.34
Sulphide, as H_2S	0.625	0.184	0.137	0.263
Thiosulphate, as S	0.053	0.063	0.026	0.051
Thiocyanate, as CNS	0.172	0.166	1.080	0.194
Phenols, as C_6H_5OH	0.048	0.0725	0.377	0.392
	Pts. per 100,000.			
Higher tar acids, O_2 absorbed ..	—	7	159	80
Oxygen absorption (4 hr. $27^\circ C.$), due to :				
Sulphide	840	247	170	354
Phenols	85	129	673	698
Thiosulphate	46	54	22	44
Thiocyanate	143	137	894	160
Difference	26	58	718	265
Total	1,140	625	2,477	1,521
Oxygen absorption, omitting sulphide	300	378	2,307	1,167
Approximate gal. per ton of coal carbonized	27	47	37	46

In continuous vertical retorts the tarry vapours containing the phenolic constituents ascend to the cooler part of the retort almost immediately they are liberated and little further decomposition takes place. The result is a liquor containing a relatively large proportion of phenol and particularly higher tar acids. In horizontal retorts, on the other hand, gases from the interior of the coal must pass to the outside of the charge and become subject to the heat of the walls of the retort before passing to the collecting main. This results in the complex phenolic constituents being decomposed into simpler substances and the higher tar acid content of the liquor subsequently produced is greatly decreased in consequence. The phenol content is somewhat reduced for the same reason. The sulphide content, on the other hand, is

usually rather greater in liquors from horizontal retorts than in those from vertical retorts, due mainly to the smaller quantity of carbon dioxide in the crude gas. Carbon dioxide and hydrogen sulphide may be regarded as competitors for the free ammonia in the liquor. Where the carbon dioxide content is low, as in horizontal retort gas, less of this substance and more hydrogen sulphide is washed from the gas into the liquor than where the carbon dioxide content is higher, as in vertical retort gas.

These differences result in the oxygen absorption of horizontal retort liquors being usually 30 to 40 per cent. less than that of vertical retort liquors, and this difference may be even greater in the resulting spent liquors from which sulphide is absent.

In coke oven practice the gases liberated from the interior of the charge are also affected by the heat of the oven walls. In this case, owing to the very high temperature of the walls, even more cracking of the phenolic compounds takes place and the resulting liquor is almost free from higher tar acids and relatively low in phenol content. At the other extreme are low-temperature carbonization systems, where the gases are subjected to practically no further heat treatment after they are liberated. Liquors from these sources are rich in higher tar acids and have a high oxygen absorption. Intermittent vertical chamber ovens produce a liquor intermediate in composition between horizontal retort and continuous vertical retort liquors.

The yield of ammonia per ton of coal carbonized in vertical retorts is generally rather greater than that obtained with horizontal retort installations. Nevertheless, owing to the greater volume of liquor produced in vertical retorts (due mainly to steaming), its ammonia content in g. per 100 c.c. is usually less than in horizontal retort liquor. This is also indicated in Table 2.

INFLUENCE OF TYPE OF COAL CARBONIZED ON THE COMPOSITION OF AMMONIACAL LIQUOR

Coals commonly used for gas production in this country do not vary greatly in their ammonia yields under the same conditions. The chlorine content of the coal, however, may vary, and this will affect the proportion of free to fixed ammonia. Some variation also occurs in the yield of phenolic bodies, although no detailed information appears to have been published. It is known that a Durham coal, for instance, carbonized in horizontal retorts, may produce a liquor almost entirely free from higher tar acids and containing very little phenol. The same coal carbonized in vertical retorts will yield a liquor whose phenol and higher tar acid content is substantially lower than would be given by, say, a Yorkshire coal similarly treated. No doubt other coking coals show

differences of the same or a smaller magnitude, but no general statement on the subject can be made. It will usually be found, however, that the composition of ammoniacal liquor is affected to a greater degree by conditions of carbonization, condensation, and scrubbing than by the nature of the coal carbonized.

QUANTITIES OF AMMONIACAL LIQUOR PRODUCED

The volume of crude ammoniacal liquor obtained per ton of coal carbonized in Gas Works practice varies considerably according to:

- (1) The amount of moisture in the coal as charged into the retorts;
- (2) The amount of water produced in the decomposition of the coal, the so-called water of constitution;
- (3) Whether steam is supplied to the charge during carbonization;
- (4) The volume of water supplied to the ammonia scrubbers.

5 per cent. of moisture in the coal, evolved without decomposition, produces 11 gal. of liquor per ton. 5 per cent. of water produced during carbonization would account for a further 11 gal. per ton. If steam to the extent of 15 per cent. of the weight of the coal is passed through the charge and 50 per cent. of this steam is decomposed, the remainder when condensed would yield 17 gal. of liquor per ton of coal. A usual quantity of water to use in the scrubbers is 10 gal. per ton of coal, although there are installations where this is greatly exceeded and a few others where by the careful use of weak liquors it is possible to dispense altogether with water in the scrubbers. There is a theoretical minimum quantity of liquor which must be produced at any cool gas temperature in order to contain all the ammonia produced; this minimum, however, cannot be reached in present day practice.

It will be seen that carbonization in continuous vertical retorts, where steaming is commonly employed, produces a greater volume of liquor than in horizontal retorts, where steam is rarely supplied to the charge.

A large number of Gas Works, particularly small ones, have no simple arrangements whereby the actual volume of liquor produced can be measured. A value accurate enough for many purposes, however, can be calculated from the total ammonia content of the liquor if it be assumed that the liquor obtained per ton of coal is equivalent to 25 lb. of pure sulphate of ammonia when the coal is carbonized in horizontal retorts, and to 30 lb. of sulphate of ammonia when

the coal is carbonized in continuous vertical retorts. The following formulæ may then be used:

For horizontal retorts the ammoniacal liquor in gal. per ton of coal carbonized is equal to 64.5 divided by the total ammonia content of the liquor in g. per 100 c.c.

For vertical retorts the ammoniacal liquor in gal. per ton of coal carbonized is equal to 77.3 divided by the total ammonia content of the liquor in g. per 100 c.c.

Using these formulæ for the liquors of composition given in Table 2 the volume per ton works out at 32.2 gal. for horizontal retorts and 51.5 gal. for continuous vertical retorts. These figures are not far from the average.

In concluding this Section it should be pointed out that the composition of an ammoniacal liquor does not necessarily remain constant once it has been produced. If air has easy access to it during storage, oxidation of sulphide and cyanide occur, with consequent increase in thiosulphate and thiocyanate content and a change of some ammonia from the free to the fixed state. Changes may also occur if the liquor is stored in contact with tar. Under these conditions a condenser liquor which has a small content of higher tar acids or a scrubber liquor which is almost free from both higher tar acids and phenols will pick up these substances from the tar and approach in these respects the composition of retort house liquor. Since, as will be shown later, it is desirable that the higher tar acid content of a liquor should be as low as possible, storage of liquor and tar in contact with each other is not advisable.

III THE RECOVERY OF AMMONIA FROM AMMONIACAL LIQUOR

It is not proposed in this Section to give a detailed account of the processes used for the recovery of ammonia from gas works liquor, since this has been done elsewhere.¹ It is more important to consider the changes which occur during these processes, with particular reference to alterations in the composition of the liquor.

Many of the smaller Gas Works now find it uneconomic to recover ammonia in any form and therefore regard the ammoniacal liquor as a waste product and as an effluent. This practice is to be deprecated, for reasons which will become apparent later; nevertheless the disposal of ammoniacal liquor as such has been investigated by the Liquor Effluents and Ammonia Committee of The Institution of Gas Engineers and will be dealt with later.

AMMONIA RECOVERY AS AMMONIUM SULPHATE

(a) "Indirect" Process

Until the last decade most Gas Works recovered the ammonia from ammoniacal liquor as ammonium sulphate, which is chiefly used as a fertilizer. The most widely used process was and is the indirect process, in which the liquor is distilled in a still of the continuous type. Steam is passed upwards through the still, meeting a stream of liquor flowing downwards. The liquor is raised to the boiling point, the ammonium carbonate and sulphide are decomposed and free ammonia is carried out of the top of the still with the uncondensed steam. In order to liberate the fixed ammonia, sufficient strong alkali, usually milk of lime or, occasionally, soda ash, is then added and the liquor further distilled. The steam-ammonia mixture, which also contains other gases, notably carbon dioxide, hydrogen sulphide, and hydrogen cyanide, leaves the still and enters a saturator containing sulphuric acid, in which ammonia is absorbed and from which solid ammonium sulphate separates. Excess steam, carbon dioxide, and hydrogen sulphide pass from the saturator through heat interchangers and condensers, the condensed water dissolving some of the other compounds such as phenols, hydrogen sulphide, etc. This condensate is known as "devil liquor". The uncondensed gases are discharged to the atmosphere after the hydrogen sulphide and cyanide have been removed by suitable means to comply with the provisions of the Alkali (etc.) Acts.

There are thus two liquid waste products from the manufacture of sulphate of ammonia by the indirect process, (i) the spent liquor leaving the still, and (ii) the devil liquor. These are usually mixed before disposal.

In some cases, where the fixed ammonia content of the

ammoniacal liquor is small or it is considered uneconomic to recover it, the liming process is omitted and the spent liquor from the still retains its original fixed ammonia.

Composition of Effluent Liquors from the Manufacture of Sulphate

During distillation almost the whole of the ammonia (or the free ammonia only, if liming is not employed), the carbon dioxide, the hydrogen sulphide and the hydrogen cyanide are removed from the liquid phase. The remaining constituents of the ammoniacal liquor are all retained either in the spent liquor from the still or in the devil liquor. Consequently the composition of the mixed waste liquors from the process can be calculated if the dilution due to the added steam is known. This varies considerably, depending on the strength of the liquor, the degree of preheating, the efficiency of the still and on whether or not the fixed ammonia is removed. As an approximation it may be taken that 100 volumes of ammoniacal liquor give rise to 150 volumes of still effluent plus devil liquor when the liming process is employed and to 135 volumes when the fixed ammonia is not recovered. On these assumptions the combined effluents from the distillation of the vertical retort liquor of the composition given in Table 2 would have the compositions set out in Table 4.

In actual practice this calculation might be reversed, both the ammoniacal liquor and the sulphate plant effluent being analysed and the dilution occurring in the process estimated from the results.

It will be seen from Table 4 that a considerable reduction in the figure for oxygen absorbed occurs during distillation, this being due partly to dilution and partly to the removal of sulphide.

It has already been pointed out that the mixed waste liquor from ammonium sulphate manufacture consists of two liquors, the spent liquor from the still and the devil liquor from the waste gas condensers. The latter provides about 15 per cent. of the total volume of the mixed liquors, the remaining 85 per cent. being spent liquor from the still. Since monohydric phenols (recorded as C_6H_5OH) are volatile in steam at $100^\circ C.$, a large proportion of these compounds passes over into the devil liquor, which is in consequence comparatively rich in phenol. Thiosulphate, thiocyanate, and higher tar acids are not readily volatilized, with the result that only traces of these substances are present in devil liquor. These points are illustrated in Table 5, which repeats the last column of Table 4 and gives, in addition, the analyses of the still effluent liquor and the devil liquor separately.

The volume of devil liquor is relatively small; its main constituent, phenol, is comparatively easily oxidized in ad-

mixture with sewage. For these reasons it is not often necessary to distinguish between spent liquor from the still and the mixture of spent liquor and devil liquor. Except where otherwise stated, where sulphate of ammonia plant effluents are referred to in this book, the term "spent liquor" is intended to include devil liquor.

(b) "Direct" and "Semi-Direct" Processes

These processes are often used on coke ovens but only occasionally on Gas Works. They accomplish the produc-

TABLE 4.—*Composition of Ammoniacal Liquor and Sulphate Plant Effluent Liquors*

	Ammoniacal Liquor.	Effluent Liquors.	
		Fixed Ammonia Recovered.	Fixed Ammonia not Recovered.
1	2	3	4
	g. per 100 c.c.		
Composition :			
Ammonia, free	1.00	—	0.01
Ammonia, fixed	0.33	—	0.25
Ammonia, total	1.50	0.02	0.38
Sulphide, as H_2S	0.15	0.01	0.01
Cyanide, as HCN	0.005	—	—
Thiosulphate, as S	0.10	0.07	0.08
Thiocyanate, as CNS	0.20	0.13	0.15
Phenols, as C_6H_5OH	0.35	0.23	0.26
	Pts. per 100,000.		
Higher tar acids, O_2 absorbed	130	87	96
Oxygen absorption (4 hr., $27^\circ C.$), due to :			
Sulphide	200	13	13
Phenols	620	409	463
Thiosulphate	85	60	68
Thiocyanate	165	108	124
Difference	580	387	430
Total	1,650	977	1,098

tion of ammonium sulphate without the previous removal of all the ammonia from the crude gas. In the direct process there is no production of ammoniacal liquor, whilst in the semi-direct only the virgin liquor occurs. Nevertheless waste liquors are produced in the processes and these are in most respects similar in composition to the effluent from an indirect sulphate plant. One point of difference is that the amounts of thiosulphate and thiocyanate are low, since in the absence of the ordinary ammonia scrubbers in the crude gas stream there is little opportunity for the oxidation of sulphide and cyanide.

AMMONIA RECOVERY AS CONCENTRATED GAS LIQUOR

In recent years there has been a growing tendency for Gas Undertakings to recover ammonia as concentrated gas liquor rather than as sulphate, the concentrated liquor being transported to some centrally-situated Works where sulphate of ammonia or other ammonia products are manufactured on a large scale. Owing to the facts that (i) the manufacture of sulphate or other ammonium salts can be carried out much more economically in large production units and (ii) the cost

TABLE 5.—*Composition of Still Effluent Liquor and Devil Liquor from Sulphate of Ammonia Plant*

	Total Waste Liquor (Fixed Ammonia not Recovered).	Still Effluent Liquor.	Devil Liquor.
1	2	3	4
Volumes	100	85	15
	g. per 100 c.c.		
Composition :			
Ammonia, free	0.01	0.01	—
Ammonia, fixed	0.25	0.30	—
Sulphide, as H ₂ S	0.01	Trace.	0.05
Thiosulphate, as S	0.08	0.09	—
Thiocyanate, as CNS	0.15	0.18	—
Phenol, as C ₆ H ₅ OH	0.26	0.17	0.75
	Pts. per 100,000.		
Higher tar acids, O ₂ absorbed	96	113	—
Oxygen absorption, 4 hr., 27° C., due to :			
Sulphide	13	1	67
Phenols	463	310	1,336
Thiosulphate	68	77	—
Thiocyanate	124	149	—
Difference	430	471	200
Total	1,098	1,008	1,603

of production of concentrated liquor is now low because of the introduction of fully automatic plants, the manufacture of the latter product is in many cases proving far more economical than that of sulphate.

Concentrated liquor is a solution in condensed steam of ammonia, carbon dioxide, and hydrogen sulphide, with smaller quantities of phenols and other bodies derived from ammoniacal liquor. The concentration of ammonia varies between 15 and 22 per cent. by weight and the carbon dioxide and hydrogen sulphide present may or may not be sufficient to convert all this ammonia into carbonate and sulphide. It is prepared from ammoniacal liquor by a distillation process similar to that used for sulphate making, with

the exception that the gases leaving the still are not passed to a saturator but are cooled and condensed, the condensate being the concentrated liquor. This process is dealt with in some detail in the Ammonia Section of this book; it is sufficient here to note that, since the whole condensate from the still is sold, there is no production of devil liquor and, therefore, the waste liquor from the process consists solely of the spent liquor from the still. In composition it is similar to the still effluent from a sulphate of ammonia plant, so that the

TABLE 6.—*Analysis of Liquors from Concentrated Gas Liquor Plant*

—	Ammoniacal Liquor to Still.	Spent Liquor.	Concentrated Liquor.
1	2	3	4
g. per 100 c.c.			
Composition:			
Ammonia, free	1.99	0.039	21.9
Ammonia, fixed	0.649	0.509	—
Sulphide, as H_2S	0.221	—	1.93
Thiosulphate, as S	0.137	0.120	—
Thiocyanate, as CNS	0.243	0.154	—
Phenols, as C_6H_5OH	0.346	0.266	0.428
Pts. per 100,000.			
Higher tar acids, O_2 absorbed	135	103	—
Oxygen absorption, 4 hr., 27° C., due to:			
Sulphide ..	298	—	2,590
Phenols ..	616	474	762
Thiosulphate	117	103	—
Thiocyanate	201	127	—
Difference	556	478	559
Total	1,788	1,182	3,911

analysis of the liquor given in Table 5, column 3, may be taken as typical. A further illustration, taken from actual Works results⁵, appears in Table 6, which gives the analyses of the ammoniacal liquor, the still effluent liquor (spent liquor), from which only the free ammonia has been removed, and the concentrated liquor itself.

RECOVERY OF AMMONIA AS AMMONIUM BICARBONATE

Patents have been taken out for a number of processes for manufacturing ammonium bicarbonate from ammoniacal liquor. These are referred to later. The effluents resulting from all these processes would differ little in quantity or composition from that from a concentrated liquor plant.

IV THE COMPOSITION AND TREATMENT OF TOWN SEWAGE

The most common method of disposal of Gas Works waste liquors is by discharge into a public sewer for subsequent treatment in admixture with sewage. It is not possible to understand the effect which gas liquor may have on sewage treatment nor the directions in which it may be desirable to modify the composition of such liquor, without a knowledge of the composition and methods of purification of sewage.

Sewage is essentially domestic liquid waste. It consists of water containing in solution or suspension inorganic salts, human wastes, soap, grease, waste food, and other organic and inorganic materials, together with the accompanying animal and vegetable life. In addition, there are often present in larger or smaller quantities trade waste waters from a great variety of manufacturing processes. Regarded from common standards sewage is a very dilute solution and suspension, its analysis always being expressed in parts per 100,000. On the other hand, its quantity is large, in English towns amounting to 25 to 35 gal. per head of population per day, and the properties of its constituents are such that only in towns situated on the sea coast or on estuaries can it be disposed of without previous treatment.

The chief reason why sewage is unsuitable for direct discharge to natural watercourses is that it contains organic substances which are decomposed, mainly by oxidation, by bacteria and other forms of life which also occur in the sewage. This oxidation, if allowed to take place in a stream or river, reduces the quantity of oxygen dissolved in the water, and this may then fall to such an extent that it cannot support aquatic life. In addition, in water denuded of its oxygen, other bacterial reactions take place, resulting in the production of foul-smelling compounds from the sewage constituents and creating unpleasant conditions generally. Theoretically there are three methods by which these undesirable effects can be avoided:

- (i) They can be prevented by destroying the life responsible for them, *i.e.*, by sterilization.
- (ii) They can be prevented by separating the oxidizable substances from the sewage before admitting it to stream or river.
- (iii) The reactions can be allowed to take place under controlled conditions before discharging the sewage to stream or river.

In Great Britain a combination of the last two methods is usually employed.

ANALYSIS OF SEWAGE

An analysis of sewage usually includes determinations of the following:

1. Ammoniacal nitrogen (or free and saline ammonia).
2. Albuminoid nitrogen (or albuminoid ammonia).
3. Suspended (settleable) solids.
4. Total solids.
5. Chlorides.
6. Oxygen absorption (O/A) from potassium permanganate.
7. Alkalinity.

The Biochemical Oxygen Demand (B.O.D.) is occasionally determined, but more often this test is used only for sewage which has undergone purification. It should, in addition, be carried out on crude sewage.

Details of the methods of analysis are not given, except those of O/A and B.O.D. (see Appendix 3). The tests are all to some extent empirical and need to be carried out by standardized methods which are, however, well established."

Ammoniacal Nitrogen

This arises partly by the decomposition of protein matter, either prior to or after admission to sewers. The ammonia is capable of undergoing bacterial oxidation, first to nitrous and then to nitric acid, which form salts with the alkalies of the sewage. This oxidation requires relatively large quantities of oxygen. However, oxidation of ammonia does not normally take place until that of other substances is almost complete, and in any case a number of days elapses before its velocity becomes appreciable in sewage mixed with water. This diminishes its importance somewhat, since after this interval of time sewage or treated sewage admitted to a river may well be out at sea or in a portion of the river where the dilution of the sewage is very great.

The estimation of the ammonia in sewage is carried out by distillation, using ammonia-free water as a diluent, and determining the ammonia in the distillate by means of Nessler solution.

Albuminoid Nitrogen

After distillation for the ammoniacal nitrogen determination, a solution of alkaline potassium permanganate is added to the residue and distillation continued. Nitrogenous organic matter is further broken up and more ammonia is given off, which is determined with Nessler reagent. The amount of this ammonia is an indication of the amount of more readily decomposable organic matter in the original sewage.

Suspended (Settleable) Solids

The object of this test is to determine how much of the polluting matter in a sewage can be separated by allowing it to settle. Owing to the fact that gas works wastes are, or should be, entirely in solution, there is no need to discuss this test.

Total Solids

This is not an important test. The difference between the total solids and the suspended solids gives the amount of dissolved solids.

Chlorides

The chloride content of sewage is also usually determined, but this is not generally of great significance from the Gas Works point of view.

Oxygen Absorption

The oxygen absorption test is used in an attempt to determine the relative amounts of oxidizable matter present in sewages. The oxidizing agent used is acidified potassium permanganate and the prescribed conditions for the test must be rigorously adhered to if comparative results are to be obtained. During the period of the test the organic matter in sewage is far from completely oxidized, so that as a measure of the actual amount of oxidizable matter present the test fails completely. For domestic sewages generally, however, the relationship of the organic matter undergoing oxidation to the total amount present is relatively constant, and in these cases the oxygen absorption test can be used to measure the relative amounts of oxidizable organic matter. The test is easy to carry out and in many cases the result is the only criterion adopted for the strength of the sewage.

Satisfactory as this may be for ordinary domestic sewage, it is inadvisable to rely on this test for determining the strength of sewages containing trade wastes or for trade wastes themselves. The fraction of organic matter in these wastes which will react with permanganate may be much greater or much less than in sewage. Examples could be given of wastes rich in organic matter of which only a very small proportion can be oxidized by potassium permanganate; others contain organic matter which under the same conditions undergoes almost complete oxidation. In these circumstances the use of the oxygen absorption test as a criterion of the strength of the waste liquor would give misleading results.

A much more satisfactory test would obviously be one in which oxidation was in all cases much more complete, and in this connexion a test⁸ in which potassium dichromate is used has much to recommend it. In this test the sewage is treated with hot concentrated sulphuric acid and potassium

dichromate, and under these more drastic conditions much more oxidation takes place. While not entirely free from the risk of giving misleading results, this test will usually give much more reliable comparisons of the "strengths" of sewages than the permanganate test.

Alkalinity

Normal domestic sewage is alkaline to methyl orange. This reserve of alkaline substances is of advantage since it allows of the oxidation of ammonia to nitrite and nitrate without giving rise to an acid reaction. Sewages containing trade wastes may have abnormal alkalinities or may in some cases have an acid reaction.

Related to the alkalinity of a liquid is its pH value which is defined as minus the logarithm to the base 10 of the hydrogen ion concentration in g. per litre. A solution of pH 7 is neutral; if the pH value is less than 7 the solution is acid and if it is greater than 7 the solution is alkaline. Domestic sewage is usually slightly on the alkaline side, having a pH value of about 8. This may be materially influenced by the presence of trade wastes. A limed spent liquor may increase the pH value slightly, depending on the amount of excess lime; unlimed spent liquor does not influence the pH value; 0.5 per cent. of an ammoniacal liquor in sewage will increase the pH value by 0.2-0.3.

Biochemical Oxygen Demand (B.O.D.)

The oxidation of the organic substances in sewage which takes place under natural conditions is not purely chemical in character, but biochemical, being accomplished by the aid of lower forms of animal and vegetable life. It follows that the best way of determining the amount of oxygen required for the purpose, and also the rate at which it is required, is to use a biochemical test in which the conditions of natural oxidation are reproduced as far as possible, rather than a chemical test such as the permanganate or even the dichromate test. Such a test is that for biochemical oxygen demand (B.O.D.). In carrying out this test sewage is mixed with diluting water containing more than sufficient dissolved oxygen for the oxidation and at least two glass-stoppered bottles are completely filled with the mixture. The concentration of dissolved oxygen in the liquid in one of the bottles is determined immediately and that in the other after allowing the bottle to stand for 5 days at 18° C. The difference between the results gives the amount of oxygen used in the reactions which have taken place during the incubation, and this is calculated as parts of oxygen per 100,000 parts of the original sewage.

This test suffers from the disadvantage that the results are not known for five days, and the result is also dependent to

some extent on the nature of the water used for dilution; nevertheless the test is the closest imitation so far devised of the natural processes of oxidation and gives most valuable information. For a more detailed study of the processes it is necessary to make oxygen determinations after different periods of incubation, and in this way the rate at which oxygen is used at various stages can be found.

STRENGTH OF SEWAGE

The analysis of a typical domestic sewage is given in Table 7:

TABLE 7.—*Analysis of Sewage*

	Pts. per 100,000.
Ammoniacal nitrogen.. .. .	3.0
Albuminoid nitrogen	1.0
Suspended solids	35.0
Total solids	100.0
Chlorides, as Cl	15.0
Alkalinity, as CaCO_3	50.0
Oxygen absorption KMnO_4	10.0
Dichromate test*	30.0
Biochemical oxygen demand.. .. .	50.0

* Carried out as described by Abbott.

Of the items in this table the total solids, chlorides, and alkalinity are largely dependent on such factors as the composition of the tap water of the district. On the basis of the remainder the strength of the sewage is assessed. Unfortunately this cannot be accurately expressed by a single figure, although various formulæ, involving the ammonia contents and the oxygen requirements, have been proposed. Frequently, however, sewage is judged on its oxygen absorption from potassium permanganate alone and some classification similar to that given in Table 8 is used:

TABLE 8.—*Oxygen Absorption of Domestic Sewage*

	Pts. per 100,000.
Strong domestic sewage	15
Average " "	10
Weak " "	

DISPOSAL OF SEWAGE

The sewage of a district is conveyed by a system of sewers either direct to the sea or estuary or to the Works where it is treated. In some places, owing to the geographical configuration of the district, it is impossible except at great expense to convey all the sewage to one point and, consequently, two or more Works are constructed to serve different parts of the same town. In other cases, and the number of these is

growing for many reasons, the sewage produced in a whole drainage area, irrespective of local political divisions, is conveyed to one large works for treatment.

Disposal by Dilution

According to the opinion expressed by the Royal Commission on Sewage Disposal,⁹ where the quantity of water into which the sewage is discharged is such that the latter is diluted at least 500 times, the sewage can be discharged without previous purification. In these cases the oxidation which occurs subsequent to the discharge does not unduly deplete the dissolved oxygen content of the mixture and little damage or nuisance is caused. Such disposal is called "disposal by dilution," and districts which may adopt it are obviously those near to the sea or near estuaries where the flow of water is exceedingly large compared with the flow of sewage. Even in such districts it is not uncommon for the foreshore or river banks to be objectionable in appearance and odour. This is due to the incomplete mixing of sewage and water, the proportion of sewage being high locally. In such places either the dissolved oxygen is completely used, facilitating odour production, or sewage sludge is deposited which begins to ferment. There is therefore a tendency for more and more of these places to install sewage purification plants.

Other districts where the available dilution for the sewage is not so great, but still exceeds 150 times, may, in the view of the Commission, discharge sewage without treatment except simple settling. The sewage is caused to flow very slowly through large tanks, allowing the larger suspended particles to be deposited as a sludge at the bottom. This removes a certain amount of putrescible matter and reduces the amount of oxidation subsequently required in the stream.

At the majority of centres of population in this country, however, the volume of water available for diluting the sewage is not great enough to allow of the latter being discharged without much more purification than is given by simple settling. There are three chief processes by which this additional purification is achieved:

- (1) Purification by land treatment;
- (2) Purification in biological filters;
- (3) Purification by activated sludge.

These methods are occasionally used in conjunction with one another and almost invariably in conjunction with settling tanks which remove most of the suspended matter from sewage.

Purification by Land Filtration

In this process sewage is applied to agricultural land. The method of application depends largely on the amount of land available and also on the type of soil, but details do not

require consideration here. In the soil, purification of the sewage is effected by oxidation and other processes not completely understood. The purified liquid is then drained away to a river or stream.

Under suitable conditions land treatment is a perfectly good method of sewage purification. It may be regarded as the oldest method of sewage disposal, but it suffers from the great disadvantage that it requires a great deal more land than is nowadays generally available at reasonable cost. Except for some of the smaller country towns and one or two larger places, the process has in this country now given place to processes which seek to accomplish more quickly and in a smaller area the purification processes which require large areas in land treatment.

Purification by Biological Filters or Bacteria Beds

The bacteria bed system of sewage purification is in use in many places in this country. The lay-out of a typical plant is shown in Figure 1. It should be remembered that, owing to the different strengths of sewage requiring treatment, to the shape and slope of the land available and to the different ideas of engineers, no two sewage works are quite the same in design or operation. The following general account must not therefore be regarded as applying in detail to any particular case

Sewage enters the works at point A and immediately passes to a relatively small tank B, through which it flows with a velocity great enough to keep the organic impurities in suspension but small enough to allow the heavier "detritus" to settle. The detritus, which is mainly mineral matter, sand, grit, etc., is not generally putrescible and can be immediately tipped or otherwise disposed of without nuisance.

The sewage leaving the detritus tanks passes through some form of metering device C to the settling tanks D. These are large and deep, shown in the diagram as rectangular in shape though sometimes circular, through which the sewage passes so as to reduce its rate of flow. In these tanks much of the matter in suspension settles out as a sludge and some purification is thus effected. Other changes also occur. The sludge is removed periodically and disposed of in a suitable manner.

From the settling tanks the sewage proceeds to a dosing chamber E, from which it gravitates to bacteria beds F. In Great Britain, these are usually about 6 ft. in depth and contain "medium" on which bacterial and other life may develop. The medium may be clinker, granite, metallurgical coke, hard coal or any other material which does not readily disintegrate and which possesses a suitable surface. The settled sewage is applied to the beds from arms fitted with jets, or from fixed jets, which distribute the liquid uniformly over the surface. Moving arms, where used, have a circular motion for circular beds and a to-and-fro motion for rec-

tangular beds, and usually derive their motive power from the sewage itself, the jets being suitably placed, but in a few cases an independent source of power is used. The sewage which is distributed over the filter percolates slowly through the filtering medium till it reaches the base, from which it gravitates to channels which conduct it to the humus tanks G. While the liquid is descending the filter, air should have free access to it so that aerobic action can take place continuously.

Domestic sewage contains within itself all the agents necessary for its purification, with the exception of oxygen, and, given sufficient time and air, will purify itself completely, as it does for instance in a river if the dilution is great enough. A bacteria bed may be regarded as a local concentration of these purifying agents which are able to carry out in the course of a few hours the work of purification which would normally take many days. The gelatinous film which accumulates on the medium composing the bed contains enormous numbers of bacteria and other organisms which, by processes involving coagulation, adsorption and oxidation, rapidly remove or oxidize objectionable constituents in sewage.

The effluent from bacteria beds should be perfectly clear, apart from comparatively large particles of a light sludge, called "humus" sludge, which is settled out in settling tanks, called humus tanks, through which the sewage flows after leaving the beds. The sewage should then be almost free from both oxidizable matter and suspended matter and should in consequence be quite fit to enter a stream or river.

Table 9 shows the composition of a weak domestic sewage at different stages of treatment in a purification system of the kind described.

TABLE 9.—*Analysis of Sewage at Different Points in a Bacteria Bed Purification System*

—	Pts. per 100,000.			
	Crude Sewage	Effluent from Settling Tanks.	Effluent from Bacteria Beds.	Effluent from Humus Tanks.
1	2	3	4	5
Ammoniacal nitrogen	4.44	4.55	0.37	0.26
Albuminoid nitrogen	0.80	0.43	0.18	0.08
Oxidized nitrogen *	0.0	0.0	3.08	3.12
Oxygen absorption	7.0	4.9	1.48	0.72
Alkalinity	52	50	23	23.6
Chloride	11.6	10.4	9.8	10.0

* Nitrite and nitrate.

In the settling tanks a reduction in oxygen absorption, due mainly to deposition of oxidizable material, takes place; in addition, the albuminoid ammonia is reduced and free and saline ammonia slightly increased by the further decomposi-

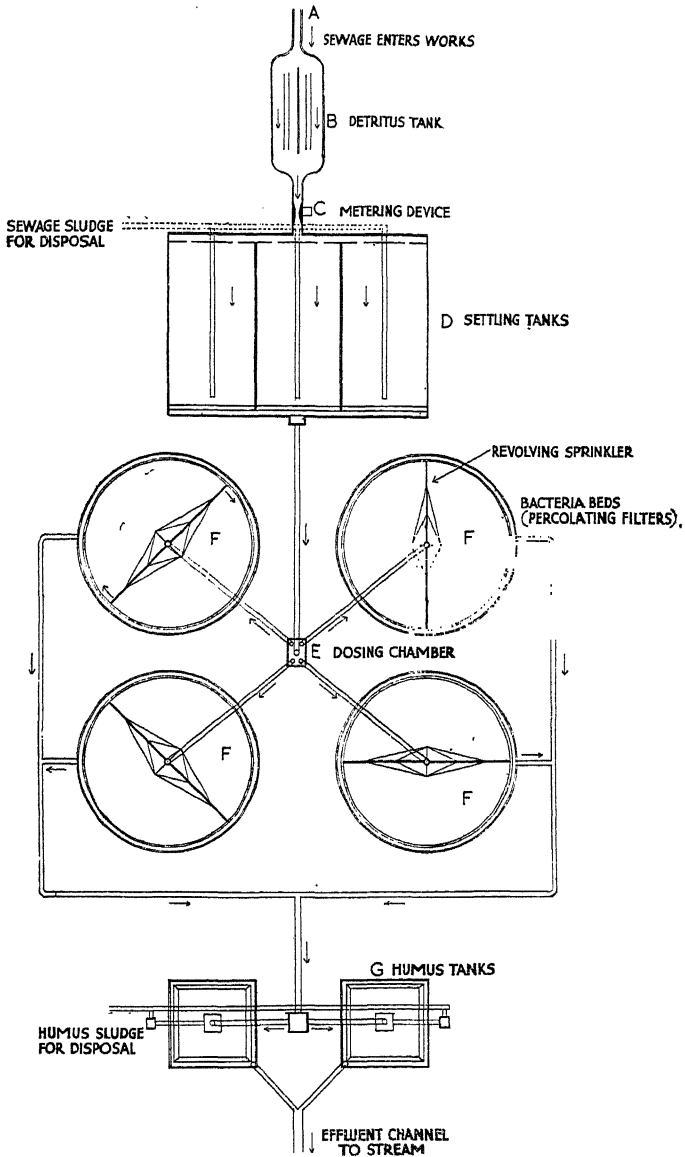


FIGURE 1.—Typical Lay-Out of Percolating Filter System for the Purification of Sewage.

tion of protein matter. In the bacteria beds the oxygen absorption is greatly diminished due to oxidation and coagulation, the albuminoid ammonia is also greatly reduced and the free and saline ammonia almost completely removed, resulting in the production of almost an equivalent quantity of oxidized nitrogen and in a reduction in alkalinity. The effluent from the humus tanks is similar in composition, except for a further reduction in oxygen absorption due to the separation of the humus sludge.

In the analyses given in Table 9 no figures for the biochemical oxygen demand were determined. The common experience is that there is a reduction in this value in the settling tanks and a very great reduction in the bacteria beds. the B.O.D. of the final effluent being no more than 2 to 5 per cent. of that of the crude sewage.

Purification by Activated Sludge

In a slowly increasing number of cases the activated sludge system of sewage purification is being adopted. It has the advantage over bacteria beds of requiring less space and of resulting in only a small loss of hydrostatic head of the sewage. Its relative disadvantages are that more power is required to run the plant and that it is more sensitive to changes of conditions. The lay-out of a typical plant is shown in Figure 2.

The preliminary treatment of the sewage, namely, separation of detritus and sewage sludge, is generally the same as with the bacteria bed system and is shown so in the diagram (A-D). On leaving the settling tanks the sewage is mixed with a small proportion, *e.g.*, 10 to 15 per cent., of "activated sludge" at E and then proceeds to the aeration tanks F. Here suitable devices ensure that the activated sludge-sewage mixture is continually aerated and agitated, and, under such conditions, rapid flocculation and oxidation of organic matter take place, and the sewage becomes clarified. The oxygen absorption falls as in bacteria beds and, if time were allowed, oxidation of ammonia would also take place. It is not often, however, that this is considered sufficiently desirable to justify the extra capacity and power needed. On leaving the aeration tanks the mixture is allowed to settle in settling tanks G, in which the sludge is deposited and from which the clear supernatant liquid is discharged as being adequately purified. At this stage the sludge is in some cases "exhausted" and is unable to effect further rapid purification without "reconditioning". For this purpose it enters the conditioning tank H, where it is aerated in the absence of sewage. It is then pumped back to E to mix with a further quantity of settled sewage. During the process there is an accumulation of activated sludge; the surplus may be led back to mix with crude sewage as it enters the settling tanks.

The reactions by which purification is effected by activated

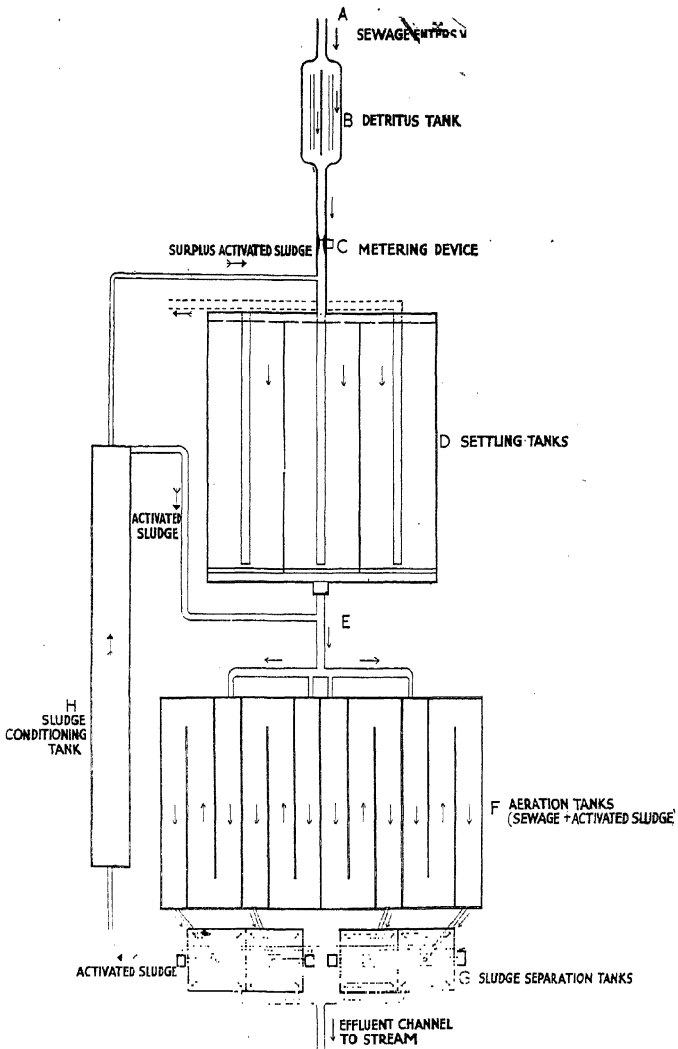


FIGURE 2.—Typical Lay-Out of Activated Sludge Plant for the Purification of Sewage.

sludge are similar in many respects to those which take place in bacteria beds. In the latter, natural purification is hastened by a huge accumulation of life supported as a jelly on the surfaces of the medium; in the former, the same accumulation takes place, unsupported, however, except by its own tendency to form "flocs."

Times of Retention

The following are approximate values for the time taken for the sewage to pass through the different parts of the sewage purification plants. Some of these are liable to great variation according to the strength of sewage and other local circumstances and must therefore be taken as illustrative only.

Detritus tanks	$\frac{1}{2}$ hr.
Settling tanks	12 hr.
Bacteria beds	2 to 4 hr.
Humus tanks	2 hr.
Activated sludge aeration tanks ..	8 to 12 hr.
Activated sludge settlement tanks ..	2 hr.

The size of the bacteria beds is such that not more than about 70 gal. of normal strength sewage are treated per day per cu.yd. of medium.

Obviously the time of retention is also dependent on the rate of flow of sewage; the larger the flow the quicker the passage through the Works and the shorter the time of retention in any particular part of the plant. The flow usually taken as standard is the average flow over 24 hours in dry weather. Plants are usually constructed to give complete treatment to sewage arriving at a rate not exceeding three times this. In times of rain the flow of sewage is greater and any in excess of three times the dry weather flow is not given complete treatment but is settled in tanks set apart for the purpose and then discharged to the river.

Disposal of Sludge

Sewage sludge deposited in the settling tanks can be a source of very offensive odours unless care is taken. In this country it is usually dried on open drying beds and then sometimes used as a fertilizer, but it is a growing practice first to submit the sludge to what is known as "anaerobic digestion". The sludge is allowed to ferment in the absence of air, when it produces a considerable volume of inflammable gas (chiefly methane), loses its liability to cause aerial nuisance and becomes easier to dry.

STANDARDS OF PURITY FOR PURIFIED SEWAGES

The object of sewage disposal is not to produce an effluent which is as good as drinking water, nor even necessarily one in which fish and other aquatic fauna and flora can live. It is to produce an effluent which can be discharged into an adjacent stream without creating objectionable conditions.

The quality of an effluent should therefore be judged in relation to the volume and quality of the water into which it is discharged. If the effluent is received into a stream which carries a large volume of water compared with the volume of effluent, then the need for a high degree of purification is not so great as in those cases where the flow of sewage exceeds that of the stream. This variation in requirement probably provides the reason why no general standards of purity have ever been legalized. The Royal Commission on Sewage Disposal, however, recommended that there should be such a general standard⁹ and, although this has never been legalized, it is in general use as a basis for determining the degree of purification to be aimed at. This standard for purified sewage is:

Suspended solids content not to exceed 3 parts per 100,000, and biochemical oxygen demand (5 days) not to exceed 2 parts per 100,000.

The Thames Conservancy¹¹ adopts the same standard for effluents discharged into most of the rivers and streams under its jurisdiction, with the addition that the albuminoid ammonia content of the effluent must not exceed 0.2 part per 100,000. The Port of London Authority has less stringent standards, since the amount of diluting water is greater in the part of the Thames under its control and it is not subsequently used for drinking water. Other River Authorities have their own standards.

It will be noticed that the only test for oxidizable matter in the recommended standard is a biochemical one. It aims, quite properly, not at determining the amount of oxidizable matter present but at the amount of oxidation which may be expected to take place in the stream after discharge. This might or might not bear any simple relation to the oxidizable matter determined by the oxygen absorption from permanganate test. In actual fact, with a well-purified effluent from the normal domestic sewage, the O/A value is usually very nearly the same as the B.O.D. value and, in a large majority of cases, it is possible to say that if the former is considerably less than 2 parts per 100,000 then the latter is also less than 2 parts per 100,000 and, conversely, if the O/A is appreciably greater than 2 the B.O.D. is also greater than 2. Now the oxygen absorption test is not only easy to carry out but the results are available quickly and, for these reasons, there has been a great tendency, particularly on small Works, to give to the O/A the significance which really belongs to the B.O.D. and to use it as almost the sole criterion of the quality of an effluent. This has been more or less justified by results where purely domestic sewage is concerned, but cannot be justified where the sewage contains trade wastes of a composition entirely different from sewage itself. Unfortunately this is not always realized.

V THE DISCHARGE OF GAS WORKS LIQUORS TO SEWERS

It has already been stated that the most common method of disposal of gas works waste liquors is by discharge into the public sewers. It would be a mistake, however, for Gas Undertakings to suppose that they have an unrestricted right to adopt this method of disposal and, equally so, on the part of Sewage Authorities to believe that they possess unrestricted power to prohibit such discharge.

THE LEGAL POSITION

Until July 1st, 1938, the right of discharge of trade waste liquors into sewers was regulated mainly by the Rivers Pollution Prevention Act of 1876, in which it is laid down that, in general, Local Authorities having sewers under their control shall allow manufacturers to discharge liquid trade wastes into them. The Local Authority is not, however, compelled to accept liquor which would prejudicially effect the sewers or the disposal of their contents, or which would be injurious from a sanitary point of view. In addition, Local Authorities cannot be compelled to accept trade wastes if the sewers or sewage treatment works are only large enough for the domestic requirements of the district. The position created by this Act was not very clear, the right to discharge or prohibit discharge being dependent on the interpretation of such phrases as "prejudicially affecting the sewers or the disposal of the sewage matter" and "sufficient for the requirements of the district." In the absence of any legal standard for purified sewage, this latter phrase is specially difficult to interpret, and no general rule can be given.

The Public Health Act, 1936 also contains sections concerning the admission of trade wastes to sewers but with regard to this matter this Act is superseded by an Act dealing solely with the admission of trade effluents to sewers, namely, the Public Health (Drainage of Trade Premises) Act, 1937, which came into full operation in July, 1938. This Act does not apply to Scotland, Northern Ireland, or to London.

The effect of the Act is that a manufacturer may discharge trade effluents into the public sewers (*a*) in accordance with the Byelaws or (*b*) with the consent of the Local Authority. Before such effluent is discharged a written notice must be served on the Local Authority, stating the nature or composition of the effluent, the maximum quantity to be discharged on any one day and the highest rate at which it is proposed to discharge. If the discharge is in accordance with the Byelaws no consent of the Local Authority will be necessary. If the discharge is not to be in accordance with the Byelaws the consent of the Local Authority may be given unconditionally or subject to the conditions specified in Section 5.2 (3) of the

Act. The consent of the Local Authority is not necessary if effluents of the same nature and composition were lawfully discharged during the year ended 3rd March, 1937, provided that the previous highest daily quantity and rate are not exceeded and provided that any payment which the manufacturer made to the Local Authority by agreement is still continued.

A Local Authority may make Byelaws under the Act and can be compelled to do so by the Ministry of Health. The Act confers upon traders the right to make objections to any proposed Byelaws, and such objections must be taken into consideration before such Byelaws are confirmed. The Local Authority must send notices they are required to publish regarding Byelaws to owners or occupiers of trade premises who register themselves for the purpose. Byelaws may be made:

- (a) Determining the period of the day when the discharge shall take place;
- (b) Requiring the exclusion of condensing water;
- (c) Requiring the elimination from the effluent of any constituent which the Authority is satisfied would injure the sewers or make specially difficult the treatment or disposal of the sewage;
- (d) Determining the maximum quantity of discharge and its highest rate;
- (e) Regulating the temperature and acidity or alkalinity;
- (f) Requiring payment for the reception of the effluent into the sewers and, also, for the provision and maintenance of sampling points and measuring devices.

It would thus appear that the Local Authority has no power to prohibit the discharge of an effluent into the sewers, but it is conceivable that the conditions it may lay down concerning quantities, composition and payment may be such as to effect virtual prohibition. Provision is made under the Act, however, for an appeal to the Minister of Health by any manufacturer aggrieved by any such conditions, and the decision of the Minister in such cases is binding on all parties.

It is obvious that, so far as gas works waste liquors are concerned, this Act cannot be administered fairly without a knowledge of the effect which the liquors may have on sewage and its treatment by various methods. It has been part of the task of the Liquor Effluents and Ammonia Committee of the Institution to ascertain any such effects and Section VI is devoted entirely to this matter.

PRACTICAL CONSIDERATIONS

There are a few simple matters which a Gas Undertaking should bear in mind when discharging waste liquor to sewers, and attention to these may in many cases make all the difference between satisfactory and unsatisfactory disposal.

Tar Separation

Spent liquors should in all cases be free from particles of tar, since tar, if not completely separated from the ammoniacal liquor fed to the still, is usually deposited there, causing endless trouble. Where ammoniacal liquor is considered waste and is admitted to the sewers it is possible, unless care is taken, for small quantities of tar to be retained in suspension. The separation of this tar is essential since (a) it contains large quantities of phenol and higher tar acids which are extracted by the sewage and (b) the deposition of tarry matter on bacteria beds and other purification media impairs their efficiency. All tar particles should therefore be removed from a liquor before the latter is discharged to the sewers and this can be accomplished by some form of separation and filtration. The liquor on its way from storage to the sewer should be passed through a vessel or vessels containing graded coke, wood wool, or other material to which tar will adhere, the material being renewed occasionally. It is essential that particles of filtering material should not be carried away by the liquor which, on leaving the filters, should be perfectly free from suspended matter.

Temperature

Spent liquor leaves the still at about 100° C. and should not be admitted to the sewers without cooling. The effect of a hot liquor entering a sewer depends, of course, on its volume relative to the flow of sewage at the point of discharge and no upper limit of temperature beyond which discharge is not permissible can therefore suit all cases. A figure of 110° F. (which has appeared in Acts of Parliament) is a reasonable one and is often insisted upon. Where a spent liquor storage tank is in use sufficient cooling may take place here; otherwise a series of cooling troughs or some such arrangement may be used. Occasionally spent liquor is mixed with cold waste liquids and this brings about the desired reduction in temperature.

Equalized Flow

It will be shown later that it is very important for effective purification that the ratio of gas works liquor to the dry weather flow of sewage should remain relatively constant. When the flow of sewage is increased by storm water the flow of waste gas liquor should not be correspondingly increased. As already explained, all sewage in excess of three times the dry weather flow is not given complete treatment, the justification for this being that it is weak and its polluting character thereby diminished. This would not be so if the flow of gas liquor were correspondingly increased at such times.

Where ammoniacal liquor is the "effluent" this constancy

of discharge is easy to arrange, since the rate at which the liquor is produced is not subject to great or rapid variation. The difference between summer and winter production can be balanced out to some extent, if the storage tank is large, by gradually emptying it during the summer and filling it during the winter.

Where concentrated liquor plants operate it is often the practice to run them as continuously as possible, thereby producing spent liquor at a constant rate. Usually, however, there are times when such plants are unavoidably shut down and to meet such contingencies it is desirable to have a storage tank of suitable size for the spent liquor. This should be kept filled when the plant is at work, being emptied at a gradually decreasing rate over a period of a week or more when the plant is shut down, thus allowing the discharge of spent liquor to the sewers to diminish gradually. When the plant is restarted the discharge to the sewer should be small at first and increased slowly to the normal, the excess produced over that discharged being used to refill the storage tank.

Where sulphate of ammonia is made at a Gas Works the plant is often worked intermittently, so that spent liquor is produced rapidly during the period of working, say, of one month, and not at all in the following period of perhaps equal length. In order to achieve an equalized discharge of effluent to the sewers in such cases it is plainly necessary to have a much larger equalizing or balancing tank for the spent liquor.

In addition to some arrangement for equalizing the daily discharge of waste liquor, it is often desirable that during each day the discharge should be roughly proportioned to the flow of sewage. If the discharge were uniform throughout the 24 hours, the ratio of liquor to sewage during the night, when the flow of sewage is small, would be abnormally high and perhaps greater than the sewage purification system could treat efficiently. The effect of this would be magnified by the fact that the night sewage, owing to its approximately 12 hours' stay in the settling tanks, passes through the oxidation part of the purification system in the daytime and its stay in this part of the plant is shortened by its rapid displacement by the incoming day sewage. Alternatively, if the sewer to which the liquor is discharged is flat or uneven, a large discharge of liquor during the night hours might accumulate in it and be pushed forward in bulk by the first flush of the early morning sewage and arrive at the purification works as a sewage containing a large proportion of gas works liquor. It is therefore advisable that during the night liquor should be admitted to the sewers, if at all, at a reduced rate. It is usually sufficient to adjust the discharge so that it is either halved in rate or cut off altogether between about 10 p.m. and 7 a.m.

Control of Discharge

It is desirable that the discharge of liquor from the Gas Works should be under strict control and therefore the use of an adjustable stop cock is not recommended unless its normal position is full open. It is preferable to use some kind of orifice which, under constant head, cannot pass more than the required amount. If this orifice can be used with a flow recorder so much the better, since the management then has evidence of what the flow was at any particular time. If the flow is cut down at night two orifices should be used, one calibrated to pass the day flow and the other the night flow. If the discharge is by pump it might be possible for this to be run at constant speed and so pass a constant amount. The details of arrangement will depend on local circumstances, but the primary aim should always be borne in mind, that is, to secure a regular discharge and to ensure that in no circumstances can the desired rate be exceeded without the knowledge of the management.

RELATIVE AMOUNTS OF GAS WORKS LIQUORS AND SEWAGE

The difficulty of treating sewage containing gas works waste liquors depends more than anything else on the amount of liquor in the sewage. This in turn depends on the system of carbonization employed, the amount of gas used in the district and on whether the areas served by the Gas Works and the sewage works to which the waste liquor is sent are approximately the same. In the majority of cases the areas served by the two undertakings are approximately the same and, where this is so, the amount of waste gas liquor is usually 0·2 to 0·5 per cent. of the amount of sewage. On the average, if ammoniacal liquor is discharged to the sewers, it amounts to 0·3 per cent. of the sewage and if spent liquor is so discharged the corresponding figure is about 0·4 per cent.

PAYMENT FOR TREATMENT OF GAS WORKS LIQUORS

It has been mentioned that the Public Health (Drainage of Trade Premises) Act, 1937, empowers Local Authorities to make Byelaws for requiring payment for the reception of trade wastes into the sewers. At the present time there is no sort of uniformity in the matter as regards gas works liquors. Many Gas Works have discharged their effluents to the sewers for a large number of years and the question of payment has never arisen; others pay what is no more than a nominal sum; and a few are required to pay an amount which can only be described as exorbitant. There is naturally a diversity of opinion on the matter.

VI THE EFFECT OF GAS WORKS LIQUORS ON SEWAGE TREATMENT

THE EFFECT OF GAS WORKS LIQUORS ON THE COMPOSITION OF SEWAGE

Knowing the analysis of any sewage and any gas works liquor, the composition of any mixture of the two can be found by calculation provided the ratio of gas works liquor to sewage is known. Table 10 repeats the analysis of a typical sewage given in Table 7 and gives, in addition, the calculated analyses of (a) the same sewage containing 0.3 per cent. of ammoniacal liquor from vertical retorts, (b) the sewage containing 0.4 per cent. of the spent liquor (including devil liquor) resulting from the recovery of the free ammonia from this ammoniacal liquor and (c) the sewage containing the same quantity of spent liquor from the recovery of all the ammonia from the ammoniacal liquor. In addition to the

TABLE 10.—*Composition of Sewage Containing Gas Works Liquors*

	Pts. per 100,000.			
	Sewage.	Sewage + 0.3 per Cent. Ammoniacal Liquor.	Sewage + 0.4 per Cent. Spent Liquor (Unlimed).	Sewage + 0.4 per Cent. Spent Liquor (Limed).
1	2	3	4	5
Ammoniacal nitrogen ..	3.0	7.5	4.5	3.0
Albuminoid nitrogen ..	1.0	1.0	1.0	1.0
Suspended solids ..	35.0	35.0	35.0	35.0
Chlorides, as HCl ..	15.0	17.7	17.6	17.1
Alkalinity, as CaCO ₃ ..	50.0	59.0	50.0	51.0
Oxygen absorption, KMnO ₄ ..	10.0	15.0	14.3	13.8
Dichromate test ..	30.0	33.5	33.0	32.5
Biochemical oxygen demand	50.0	53.0	53.0	52.0
Phenols	—	1.1	1.1	1.0
Thiosulphate	—	0.3	0.3	0.3
Thiocyanate	—	0.6	0.6	0.5

usual determinations made on sewage, the concentrations of phenols, thiosulphate and thiocyanate in the sewage-liquor mixtures are also given.

It will be seen that the greatest difference between the effect of ammoniacal and of spent liquor is that the latter has little influence on the ammoniacal nitrogen content and none on the alkalinity, whereas the former considerably increases both these values. The important effect of spent liquor is that the oxygen absorption, as measured by the permanganate test, is considerably increased. Since this, as has been explained, is commonly used as an index of the strength of sewage, it is not surprising that gas liquor has often been regarded as a very objectionable constituent. But this conclusion is not sup-

ported by either the dichromate test, which is a much better measure of the amount of oxidizable organic matter present, or the biochemical oxygen demand, which, as a biochemical test, is much to be preferred for a liquor which has to undergo biochemical oxidation. Potassium permanganate only attacks a small proportion of the oxidizable matter in sewage, whereas it oxidizes the greater part of that in gas works liquor.

To a certain extent the reverse happens in the dichromate test, since the organic matter in sewage is almost completely oxidized, whereas the phenols in gas works liquor are lost by volatilization before oxidation begins. These facts demonstrate that the results of adding gas works liquor to sewage cannot be assessed by analysis alone (indeed, simple analysis may lead to quite wrong conclusions), but must be judged by the effect (*a*) on the purification processes, if any, to which the sewage is subjected and (*b*) on the stream into which the sewage or purified sewage is ultimately discharged. Analysis is only useful when it can be related to these practical matters.

EFFECT OF GAS LIQUORS ON THE DISPOSAL OF SEWAGE BY DILUTION

Where the sewage is admitted to a stream without biological treatment the presence of a trade waste in solution in the sewage may be harmful in two ways. It may have a specific toxic effect on fish living in the stream or animals drinking from it; or its oxidation may deplete the dissolved oxygen content of the water.

Toxicity of Gas Works Liquors

Most of the constituents of ammoniacal and spent liquors are toxic to fish. The concentrations of those constituents which have fatal effects vary with the kind of fish, the tem-

TABLE 11.—*Concentrations of Gas Works Liquors*

Phenols	1	part per 100,000
Higher tar acids (catechol)	1	
Ammonia (uncombined, not as carbonates)	1	
Ammonium salts	50	
Thiocyanate	20	
Cyanide	1	in several million
Pyridine	40	per 100,000
Naphthalene	0.5	

perature of the water and the condition of the water apart from these constituents. A number of investigations on the matter have been carried out¹² and figures for lethal doses under different conditions determined. The figures given in Table 11 are concentrations above which marked evidence of toxic effects may be expected.

Of these, phenols and higher tar acids are very toxic sub-

stances and are contained in relatively large quantities in gas works liquors. In sewage containing gas works liquor, according to Table 10, the concentration of phenol averages about 1 part per 100,000, and the combined phenols and higher tar acids about double this amount. Sewage should not be discharged untreated unless the amount of diluting water is at least 150 times the volume of sewage. The concentration of phenols and higher tar acids in the resulting mixture works out at about one part in seven millions, a quantity much below the lethal dose. One would not therefore expect any toxic effect on fish due to gas liquor when this is mixed with sewage in normal proportions and the sewage discharged to a stream untreated.

It is a fact that the most toxic substance of those given in Table 11, namely, cyanide, is absent from spent liquors and present only in traces in ammoniacal liquor. Even where the latter is discharged to the sewers, owing to the reaction between cyanide, sulphide and oxygen, producing thiocyanate, it is very doubtful if any cyanide, as such, could reach the point where the sewage is admitted to the stream, but even were this not so the dilution effected by sewage and stream would be sufficient to bring down the concentration to well below the lethal dose.

Reactions Occurring in Water to which Sewage containing Gas Works Liquor is Discharged

The second possible effect of gas works liquor in sewage which is discharged untreated to a stream is that the oxidation of the liquor might add considerably to the oxygen requirements of the sewage. The figures given for the biochemical oxygen demand in Table 10 suggest that this is not so, since the increments due to gas works liquors were relatively very small. This has been confirmed by more detailed investigation carried out by the Liquor Effluents and Ammonia Committee of the Institution.¹⁴

Experiments which compared the behaviour, when diluted with a large volume of water containing dissolved oxygen, of sewage and the same sewage containing sufficient phenol and catechol (representing higher tar acids) to increase the oxygen absorption by 20 parts per 100,000, showed that these substances were rapidly oxidized. With phenol the process was completed in about 2 days at 18° C. and with catechol about 90 per cent. of the possible oxidation occurred in the same time. The amount of oxygen consumed in the process was approximately equal to that consumed from permanganate in the oxygen absorption test. A similar test carried out with sewage containing thiocyanate showed that this substance remained unchanged for 8 days at 18° C. but was completely oxidized during the following four days. Ammonia as ammonium carbonate remained unchanged for at least 9 days

but was afterwards converted first to nitrite and then to nitrate. None of these substances appeared to have any retarding effect on the oxidation of the sewage which proceeded concurrently.

Similar tests were carried out with sewage containing gas works liquors and the nature of the results obtained is indicated by the fact that in order to secure effects which could be measured with any degree of accuracy the amount of liquors in the sewage had to be increased to many times the normal. The results have been averaged and re-calculated in Table 12 to refer to sewage containing 0·3 per cent. ammoniacal liquor and 0·4 per cent. spent liquor. The liquors were mixtures of liquors produced by horizontal and vertical retorts.

TABLE 12.—*Oxidation of Sewage by Dilution ; Effect of Ammoniacal and Spent Liquors*

	Pts. per 100,000 after Dilution Multiplied by Degree of Dilution		
	Sewage.	Increases caused by	
		0·3 Per Cent. Ammoniacal Liquor.	0·4 Per Cent. Spent Liquor.
1	2	3	4
Oxygen absorption :			
Initial	8·8	4·4	3·5
After 1 day	5·3	3·3	2·4
After 2 days	4·8	1·7	1·7
After 3 days	4·2	1·5	1·2
After 5 days	4·0	1·6	1·5
Dissolved oxygen used :			
Up to 1 day	12·0	0·4	0·9
Up to 2 days	22·3	1·2	1·1
Up to 3 days	33·2	2·0	1·2
Up to 5 days	45·6	1·0	1·0

In the first part of this table are shown the oxygen absorptions (permanganate test) of the sewage (re-calculated from the diluted mixture to the original sewage) and the increases in the oxygen absorptions attributable to gas works liquors immediately on mixing and at the end of periods of incubation at 18° C. of up to 5 days. The decrease with time in the oxygen absorption of the sewage is a rough measure of the amount of purification taking place due to oxidation on standing. The decrease in the oxygen absorptions due to gas works liquors is a similar measure. The values for sewage and liquors may not, however, be compared directly with each other, owing to the limitations of the oxygen absorption test which have been previously pointed out and which are

apparent in the table. The second part of Table 12 gives the amount of dissolved oxygen consumed by the sewage and the additional amount used by the gas works liquors.

The oxygen absorption due to gas liquors decreased to less than half of its original value during the first two days, the substances oxidized being sulphide (in the case of ammoniacal liquor), phenols, some of the higher tar acids and thiosulphate. The remaining constituents, thiocyanate and some higher tar acids, are oxidized only after a considerable period of incubation, and between two and five days there was no significant decrease in the oxygen absorption due to the liquors. The amount of dissolved oxygen used attributable to the gas works liquors was in all cases very small in comparison with that used by the sewage itself and for all practical purposes it may be taken as negligible.

In no experiment was there any evidence that the presence of gas works liquors in normal proportions delayed or in any way influenced the oxidation of sewage in these dilute solutions. It may therefore be concluded that, in towns so situated that the sewage can satisfactorily be discharged to a stream without prior bacteriological treatment, admission of gas works liquors to the sewers under controlled conditions should cause no difficulty.

EFFECT OF GAS WORKS LIQUORS ON THE SETTLING OF SEWAGE

So far as is known it has never been suggested that gas works liquors have any deleterious effect on the sedimentation of crude sewage. Direct experiments with normal proportions of the liquors in sewage have indicated that there is no such effect.¹⁵ the main processes occurring in the settling tanks being uninfluenced.

EFFECT OF GAS WORKS LIQUORS ON THE TREATMENT OF SEWAGE ON PERCOLATING FILTERS

Frequently sewage, after settling, is further purified by biological oxidation on percolating filters, or bacteria beds, the functions of which have already been described. The reactions occurring therein are largely oxidation processes analogous to those taking place in a stream which has received untreated sewage. It does not follow, however, that the B.O.D. test, which gives an excellent indication of the effect of sewage on a stream, will be an equally good measure of the effect of sewage on biological filters. One reason for this is that the oxidation processes occurring in the beds proceed much nearer to completion than in the 5 days of the B.O.D. test; another is that in a bacteria bed there is preferential breeding of bacteria and other organisms specially suited to the sewage supplied to it, making the filter more efficient and rendering possible reactions which would not

normally occur during the B.O.D. test. Nevertheless, if it were necessary to judge the behaviour of a sewage on bacteria beds from any single analytical test, the B.O.D. would be the most suitable.

Of the constituents of gas works liquors, phenol and thiocyanate have long been known to be susceptible to biological oxidation on bacteria beds.¹⁶ It has since been shown¹⁷ that phenol can be oxidized by any bacteria bed dealing with a normal sewage, but with thiocyanate oxidation does not take place until certain types of bacteria have developed in sufficient numbers.¹⁸ This provides one reason why gas works liquor should not be discharged to sewers intermittently but continuously, so as to maintain an adequate supply of thiocyanate bacteria in the purification system. Sulphide and thiosulphate have also been shown to be easily oxidized in bacteria beds, although the maximum concentration tolerated is smaller than for phenol and thiocyanate. Catechol is also very easily oxidized, but some other substances included under the term "higher tar acids" appear to be very resistant to attack. Ammonia, free or fixed, is also oxidizable, although the oxidation only takes place in the later stages of the treatment.

A number of laboratory investigations and one series of large scale tests have been carried out by the Liquor Effluents and Ammonia Committee on the treatment on bacteria beds of gas works liquors in admixture with sewage.¹⁹ It is not necessary to recount these. The experimental method was as follows: Several bacteria beds of similar dimensions and construction were obtained in the same condition, *i.e.*, they produced identical effluents from identical sewages. To one of these beds sewage was fed; to others was supplied at the same rate the same sewage mixed with various kinds and proportions of gas works liquors. The effluents from these beds were compared with that from the bed treating sewage alone and any difference was attributed to gas works liquor. This method of testing is particularly suitable for laboratory work, and in certain circumstances it can be used for large scale tests. The alternative method of testing, in which the sewage supplied to a single purification system is free from gas works liquor during one part of the test and contains it in another, the results of the two periods being compared, is open to many objections, although it has given useful results.

In the upper portions of a bacteria bed coagulation and oxidation of the organic matter in sewage take place and both the oxygen absorption and the biochemical oxygen demand, particularly the latter, are diminished in consequence. The investigations described above showed that, when gas works liquors are present in the sewage in normal proportions, those constituents of the liquors which react with potassium permanganate and which therefore contribute to the oxygen absorption are also largely oxidized in this portion of the bed.

These are the phenols, the thiosulphate, some of the higher tar acids and, if the bed is in suitable condition, the thiocyanate. There has been no evidence that these reactions occur at the expense of the oxidation of the sewage matter, which takes place concurrently. The oxygen absorption due to gas works liquors is greatly diminished at this stage and, as in untreated sewage, the effect of the liquors on the biochemical oxygen demand is small. So far little oxidation of ammonia has occurred and none takes place during the five days of the B.O.D. test on sewage purified to this extent, so that up to this stage the ammonia content of the ammoniacal or spent liquor is unimportant unless the amount of free ammonia is so great as to exhibit toxic qualities towards the life in the beds.

As sewage progresses further down the bacteria bed, oxidation of ammonia commences, producing nitrite and then nitrate. With sewage alone the velocity of the conversion of nitrite to nitrate is such that little of the former accumulates. Organic matter is still further oxidized and there is a further slight drop in the oxygen absorption. The biochemical oxygen demand also falls, since during the five days of the test little further oxidation of ammonia occurs. When gas works liquors are present oxidation of ammonia also takes place at this stage, but the accumulation of nitrite may be rather greater, particularly with ammoniacal liquor. Little further oxidation of the organic constituents of the liquors takes place, the oxygen absorption attributable to them diminishing only slightly. The influence of the gas liquors on the biochemical oxygen demand still remains approximately the same.

The amount of purification of the sewage occurring up to this stage is such that the purified liquid would not yet pass the test recommended by the Royal Commission and adopted by various River Authorities, the biochemical oxygen demand in general still exceeding 2.0 parts per 100,000. Before this value can be reached it is usually necessary for the oxidation of ammonia to be almost completed. By this time both the oxygen absorption and the biochemical oxygen demand of the treated sewage are reduced to below 2.0 parts per 100,000 and the amounts of organic matter and ammonia still requiring oxidation are small. With the same sewage containing a proportion of gas works liquor oxidation of ammonia may not be complete if the liquor contained much ammonia, free or fixed, and the biochemical oxygen demand may still exceed 2.0. The reason for this is not that any further oxidation of organic matter takes place in the B.O.D. test, but that oxidation of ammonia may now occur during this test. This indicates the importance of discharging to the sewers a liquor containing as little total ammonia as possible and therefore that it is far better to discharge spent liquor than ammoniacal liquor. During this last stage of bacteria bed treatment the

remaining organic constituents of gas liquor are not oxidized and the oxygen absorption due to the liquor is not further reduced. These substances are evidently very resistant to oxidation; this means that they cannot influence the biochemical oxygen demand.

No single set of experiments carried out illustrates all the effects just described. In Table 13, however, figures have been extracted from the results of two entirely separate series of trials and between them these show that the purification processes are in accordance with the mechanism just described.

TABLE 13.—*Treatment of Sewage and Sewage Containing Gas Works Liquors on Sectional Bacteria Beds*²⁰
A—Oxygen Absorption

—	Pts. per 100,000		
	Sewage.	Increases caused by	
		0.5 Per Cent. Spent Liquor.	0.4 Per Cent. Ammoniacal Liquor.
1	2	3	4
Sewage fed to beds	7.36	3.16	4.58
Effluent : Section 1	2.72	1.18	1.43
" " 2	2.40	1.00	1.17
" " 3	2.05	0.84	1.06
" " 4	1.67	0.80	1.06
" " 5	1.44	0.74	0.99

B—B.O.D. and Ammonia Contents

—	Pts. per 100,000		
	Sewage.	Increases caused by	
		0.5 Per Cent. Spent Liquor.	0.5 Per Cent. Ammoniacal Liquor.
1	2	3	4
Biochemical Oxygen Demand :			
Effluent : Section 1	10.2	1.6	1.8
" " 3	4.1	0.0	0.0
" " 5	1.47	0.42	0.69
Ammonia contents :			
Effluent : Section 1	5.2	1.5	2.8
" " 3	2.9	1.6	4.4
" " 5	0.1	1.9	4.0

In this table the important points to note are that :

- (i) The oxygen absorption of the sewage diminishes first rapidly and then more slowly.

- (ii) The oxygen absorption due to the liquors diminishes at first rapidly and then very slowly indeed.
- (iii) The B.O.D. attributable to liquors is first small in relation to that of the sewage, then negligible (since the easily oxidizable substances are now oxidized) and finally becomes appreciable again when the ammonia in the sewage has been almost completely oxidized but that in the sewage liquor mixtures has not.

A further word must be said about the biochemical oxygen demand test. It does not follow that effluents having the same B.O.D. will have the same detrimental effect on a stream. One effluent may have the greater part of its oxygen demand on the first day, when the degree to which it is diluted in the stream may be low. An effluent of this type is much less desirable than one which has the same 5-day demand but which has the greater part of it on the fifth day, after which time in the stream the dilution must be bigger and may be very much bigger. Where the presence of gas works liquors in sewage has been found to increase the B.O.D. of the effluent the increase is largely in the later stages of the incubation and is therefore not so significant as if it occurred earlier. The B.O.D. test may therefore tend to exaggerate the effect a gas liquor will have on a stream if the liquor is mixed with sewage and purified on bacteria beds.

The results of these tests may be summarized as follows:

During the passage through bacteria beds a large proportion of those substances contributing to the oxygen absorption of gas works liquors is rapidly oxidized. The remainder is very resistant to oxidation and therefore adds to the oxygen absorption of the purified effluent. It does not, however, affect the biochemical oxygen demand. The ammonia content of the liquors may or may not be completely oxidized, depending on the proportion and composition of the liquor in relation to the capacity of the filters. Any ammonia remaining after treatment may affect the biochemical oxygen demand of the effluent.

It must be borne in mind that this account of what happens when a sewage containing gas works liquors is treated on bacteria beds is a general one and is not necessarily true in detail for any particular sewage works. It is important to recognize that no two sewages are exactly the same in composition, no two purification works are identical, and the bacterial population of filters may vary from place to place. Consequently, in considering any particular scheme, the above generalizations must be applied in conjunction with a knowledge of any local peculiarities.

Conclusions.—When a spent liquor is discharged to sewers and the sewage subsequently treated in percolating filters it may be expected that the oxygen absorption of the purified effluent will show an increase due to the presence of the

liquor. This increase will be relatively small and will be caused mainly by some of the higher tar acids which are resistant to biological oxidation. It may also be partly caused by thiocyanate if the discharge of liquor to the sewers is not regular. Where the oxygen absorption is taken as the chief criterion of the character of an effluent, it is therefore desirable that amounts of higher tar acids and thiocyanate in the liquor should be reduced to a minimum. If fixed ammonia is retained in the liquor this may or may not be completely oxidized in the filters. If it is completely oxidized, the B.O.D. of the final effluent should show no increase due to the liquor. If oxidation is incomplete the B.O.D. may show an increase, but the increased oxygen demand occurs largely in the later stages of the test for B.O.D. It is, therefore, desirable that the amount of fixed ammonia in the liquor should be kept as low as possible, and this provides a further reason for reducing the thiocyanate content. Thiocyanate not only provides an acid radical for the ammonia but also, on oxidation in the bacteria beds, gives ammonium sulphate and in this indirect way increases the ammonia content of the sewage.

The behaviour of ammoniacal liquor treated on bacteria beds in admixture with sewage will be similar in many respects to that of spent liquor, but two important differences may be apparent:

- (i) For some reason, not fully understood, the quantity of nitrite in the effluent may be much larger than normal and, since nitrite is attacked by potassium permanganate, the oxygen absorption may be correspondingly increased. If the reason for this increase is not appreciated by the Sewage Authority, undue significance may be attached to it.
- (ii) Owing to the relatively high ammonia content of ammoniacal liquor, all the ammonia may not be oxidized in the beds and that remaining unchanged may adversely influence the B.O.D. value. Ammoniacal liquor in sewage adds to the work required of a bacteria bed system to a much greater degree than does a corresponding amount of spent liquor.

EFFECT OF GAS WORKS LIQUORS ON THE TREATMENT OF SEWAGE BY ACTIVATED SLUDGE

It has been previously explained that the processes occurring during the treatment of sewage with activated sludge are similar in principle to those taking place on a bacteria bed. So far as the purpose in hand is concerned there are two important differences.

- (1) Whereas in a bacteria bed the purifying organisms are to a certain extent segregated, those at the top being in perpetual contact with crude sewage and those lower down continually

dealing with a partially purified liquid, in the activated sludge process all the organisms are at first in contact with crude sewage and later have to deal with the same sewage which has undergone partial oxidation. It follows that if any trade waste has a slight toxic effect on lower forms of life this effect will be felt by all the activated sludge, whereas it may have an effect on the life in the top section of a bacteria bed but not in subsequent sections where a certain amount of

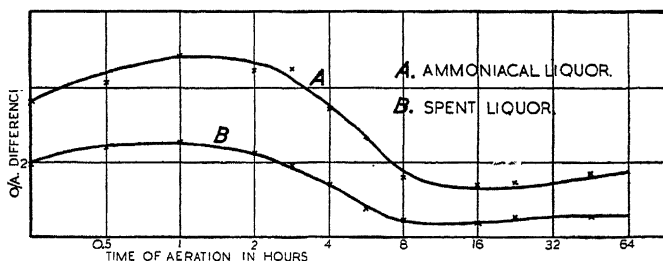


FIGURE 3.—Increases due to presence of 0.5 per cent. Ammoniacal and Spent Liquors in O/A of Sewage during Purification by Activated Sludge.

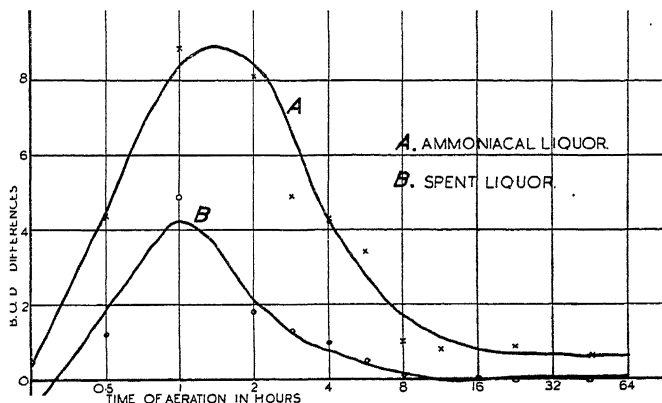


FIGURE 4.—Increases due to presence of 0.5 per cent. Ammoniacal and Spent Liquor in B.O.D. of Sewage during Purification by Activated Sludge.

oxidation has already taken place. Bacteria in activated sludge may thus be more sensitive to constituents foreign to a normal domestic sewage than those in bacteria beds.

(2) In many cases it is not necessary with the activated sludge process to effect oxidation of ammonia in order to

obtain an effluent conforming with the usual requirements. The presence of ammonium compounds in sewage undergoing such treatment is not therefore in itself of great importance, since their oxidation will not take place until the effluent has been in the stream more than five days.

From (2) it might be argued that an ammoniacal liquor mixed with sewage could be treated with activated sludge as easily as a spent liquor so mixed, and this would doubtless be the case (in the absence of sulphide) were it not that a slight toxic effect, not noticeable on bacteria beds, becomes of greater importance with activated sludge, as indicated in (1).

It has been established²¹ that the order of oxidizability of the chief constituents of gas works liquors is the same with activated sludge as on bacteria beds. Phenol and catechol are easily and completely dealt with, while some higher tar acids are very resistant to oxidation. Thiocyanate also resists oxidation until sufficient special bacteria have been induced to grow, after which large quantities can be dealt with in a short time. Sulphide is also easily oxidized, probably by chemical, not biochemical, means, but the limit of tolerance of the sludge for this compound is low, although higher than concentrations which would normally occur in ammoniacal liquor-sewage mixtures. Ammonium salts are not usually oxidized in the normal aeration period, except with special sludges, but, as explained above, this is not normally required.

In order to illustrate the effect of the presence of ammoniacal and spent liquors on the activated sludge process, the results of experimental determinations on the laboratory scale²² are given in Table 14 and shown diagrammatically in Figures 3 and 4. These experiments were carried out with liquors free from thiocyanate and thiosulphate, but the general effects were not altered by this. The first half of the table refers to oxygen absorptions and gives, after various times of aeration, (a) the O/A of sewage, (b) the increase in O/A due to the presence in the sewage of 0.6 per cent. of spent liquor and (c) the increase due to the presence of the same quantity of ammoniacal liquor. The second half of the table relates to determination of B.O.D. and is constructed similarly.

It will be seen that aeration accomplished a progressive reduction in both the O/A and B.O.D. of the sewage, so that at the end of 24 hours neither of these determinations gave results exceeding 2 parts per 100,000. The increases in these quantities caused by the presence of liquors did not, however, decrease continuously. With spent liquor each of them showed an increase during the first hour. This could only have been due to a slowing down of the rate of oxidation of the sewage itself due to a slight antiseptic effect of the liquor. After this, however, the B.O.D. attributable to the liquor diminished rapidly and after 8 hours practically disappeared, so that from an examination of the B.O.D. results it was

impossible to detect that spent liquor had been present. The antiseptic effect of the liquor had completely disappeared, the oxidizable constituents had been oxidized and the remainder had no effect on the B.O.D. The O/A due to the liquor had also begun to diminish after an hour's aeration and continued to do so until it reached but one quarter of the original in about 8 hours, after which further diminution was negligible. With the exception of the slight toxic effect at the beginning and the entire disappearance of the B.O.D. due to liquor towards the end, the behaviour of the liquor was comparable with its behaviour on bacteria beds. The zero influence on the B.O.D. was due to the fact that no oxidation of ammonia took place and therefore the additional ammonia (fixed) in the liquor was of no effect.

The toxic effect of ammoniacal liquor was much more marked, both the O/A and B.O.D. due to the liquor increasing considerably during the first two hours' aeration. This

TABLE 14.—*The Oxidation of Sewage Containing 0.6 per cent. Gas Works Liquors by Aeration with Activated Sludge*

Time of Aeration, Hr.	Pts. per 100,000.					
	Oxygen Absorptions.			Biochemical Oxygen Demands.		
	Sewage.	Increase Due to		Sewage.	Increase Due to	
		Spent Liquor.	Ammoniacal Liquor.		Spent Liquor.	Ammoniacal Liquor.
1	2	3	4	5	6	7
0	9.88	1.97	3.67	34.6	—0.8	0.4
0.5	6.68	2.43	4.12	22.3	1.2	4.3
1	5.55	2.55	4.82	12.7	4.9	8.9
2	4.05	2.22	4.47	9.1	1.8	8.1
3	3.28	1.92	4.59	6.6	1.3	4.9
4	3.25	1.41	3.43	5.6	1.0	4.3
6	2.72	0.75	2.63	3.9	0.5	3.4
8	2.43	0.45	1.60	3.6	0.1	1.0
12	2.20	0.55	1.43	2.46	—0.70	0.80
16	2.41	0.34	1.11	1.74	0	1.86
20	2.26	0.61	1.60	2.68	—0.30	0.84
24	1.98	0.57	1.47	1.37	0.06	0.97
48	1.78	0.61	1.72	1.29	0.02	0.66

toxic effect must in some way have been connected with its free ammonia content. Later, the B.O.D. due to the liquor decreased greatly, but remained of considerable magnitude relative to that of the sewage, even after 48 hours' aeration. Also the O/A due to the liquor did not diminish to such an extent as it did for spent liquor. It was quite evident that ammoniacal liquor was not so readily dealt with by the sludge as was spent liquor and this conclusion appears to hold generally, although the differences would be smaller with smaller and more normal liquor-sewage ratios.

The above experiments were carried out under such conditions that oxidation of ammonia did not take place to any appreciable extent and it has previously been pointed out that this is the most common case in practice. When the sludge is in such a condition that nitrifying organisms are active, the effect of gas works liquors is rather more complex.²⁰ In general they retard but do not prevent nitrification. With sewage alone, not containing gas liquors, a final effluent may be produced in which nitrification is in active progress. As a result, this final effluent has a relatively large O/A and B.O.D. With sludge in a corresponding condition, a sewage-liquor mixture may produce an effluent in which nitrification has not started and in consequence both the O/A and B.O.D. of this may be less than that of the effluent from the sewage alone. The exact reverse may be the case if the sludge is such that nitrification of the sewage is complete but that of the sewage-liquor mixture only partial. Then the O/A and B.O.D. of the effluent from the sewage will be low and those of the effluent from the sewage-liquor mixture high. In these cases it is therefore not always possible to forecast what the effect of gas works liquors will be.

Generally, however, it may be said that an average dose of spent liquor can readily be treated by activated sludge. It may cause a slight delay in the initial stages of purification but this will disappear when the sewage is sufficiently well purified. At this stage the presence of spent liquor will increase the O/A of the effluent to some extent, but will have little, if any, influence on the B.O.D. Ammoniacal liquor is less readily treated, having a greater retarding effect initially, a greater final effect on the O/A and an appreciable effect on the B.O.D. Such results may only be expected when the concentration of gas liquors in sewage is reasonably constant over considerable periods. Variation in the rate of discharge will lead to less satisfactory treatment, partly because efficient oxidation of thiocyanate requires a constant ratio of liquor to sewage and partly because of the great sensitivity of activated sludge to changes in the composition of the sewage. Results obtained by W. Watson,²¹ which are less satisfactory than those given in Table 14, are thought to be due to the fact that at the time of the tests gas works liquor was being received into the sewers intermittently.

EFFECT OF GAS WORKS LIQUORS ON THE TREATMENT OF SEWAGE WITH CHEMICALS

The purification of sewage by chemical methods is generally understood to mean the addition to sewage of substances to precipitate most or all of the suspended and colloidal matter, which is then separated, leaving a clarified liquid. In the early days of sewage treatment, chemical methods were tried in many places, but they generally gave place to the biological methods which are in general use in this country

today. In places where precipitants are now employed it is usually only as an adjunct to bacteria bed or activated sludge treatment, and the process was not therefore described in detail in Section IV. The reasons for the chemical method of treatment having fallen into disfavour are often stated to have been an incomplete understanding of the reactions occurring and the high cost of chemicals.

During the last few years, however, there has been a revival of interest in the method, especially in the United States of America, where many processes are now being developed, and it is claimed that purification can be accomplished with smaller installation and operating costs than with the more common biological methods. The sludge produced is also stated to be denser and easier to dispose of. In view of the possibility that chemical treatment may in the future be more widely adopted in this country, it is desirable that an account should be included here of chemical processes and of the effect of gas works liquors on them.

Chemical precipitation involves the mixing with the sewage of a solution of a metallic salt, usually trivalent, possibly adding milk of lime to increase the alkalinity, agitating the mixture to promote flocculation and finally settling out the precipitated colloids. The ferric (Fe^{+++}) ion has been found to be most effective, consistent with reasonable cost, and it is used in most of the modern processes. Where an alkali is added, lime is used. Sometimes, too, some insoluble matter like paper pulp is added. In one process a ferrous salt is employed and chlorine added to oxidize it to the ferric state and at the same time partly to chlorinate the sewage. In place of the iron salt, aluminium sulphate or chloride is sometimes used, and magnesium salts have also been suggested, though they do not appear to be generally very effective. In one process chemical precipitation is followed by treatment with zeolite, which removes the ammonia from the sewage, and in this case the total purification which is effected is claimed to be as good as would be obtained with activated sludge or bacteria beds. Generally, however, the result of chemical treatment is to produce an effluent which is intermediate in quality between a sewage which has been merely settled and one which has been treated by biological means.

Gas works liquors do not contain matter in suspension and would therefore not be expected to be precipitated by chemicals of the usual type employed. Experiment²⁵ has shown that this is so. The oxygen absorption attributable to gas works liquors in a mixture of these with sewage is unaffected by treatment with ferric salts, aluminium salts, lime or mixtures of these. The biochemical oxygen demand due to the liquors does, however, appear to be diminished by treatment with chemicals.

The precipitants usually employed in processes of chemical treatment, namely, ferric chloride and lime, are liable to pro-

duce intense colours in the presence of even dilute solutions of gas works liquors and, although innocuous discoloration is legally not pollution, it is undoubtedly a great disadvantage in any process claiming to purify sewage. The extent of colour formation depends to some extent on the composition of the liquors present, but from experiments just quoted the following general observations were made:

Mixtures of spent liquor with sewage, treated with lime and not with ferric chloride, gave a yellow-red colour which varied with the amount of lime and became more intense during the settling period. Treatment with ferric chloride alone gave solutions which absorbed light generally and which appeared quite black in depths of 6 in. or more. Mixtures treated with both lime and ferric chloride produced a very deep yellow-red colour, while alum produced no colour. Ammoniacal liquor mixtures with lime produced no colour; with ferric chloride a black was produced and with ferric chloride and lime together a very dark red colour appeared. Alum again resulted in no colour production.

The explanation of the production of these colours is simple. The effect of lime is to increase the alkalinity of the solution and in consequence the rapidity of the oxidation of higher tar acids, the products being highly coloured. Ferric chloride also reacts with higher tar acids, producing coloured bodies of unknown composition; it also reacts with sulphide, producing ferrous sulphide which, in the presence of sewage, remains in colloidal suspension as a black material. Thus colour production is bound up with the presence of higher tar acids in the case of spent liquor and with that of higher tar acids and sulphide in the case of ammoniacal liquor. Liquors free from these substances would doubtless yield almost colourless liquids when treated with chemicals.

It is possible that in this country processes of chemical treatment of sewage will be developed as a preliminary to biological treatment. By this is meant the addition of chemicals to the crude sewage, settling out the precipitated sludge and then feeding the clarified sewage to some biological treatment plant at a rate much greater than is usual without the chemical treatment. At the present time such a system is operated in several places, particularly where the sewage has a high content of colloids.

In these circumstances it appears that gas works liquors would still cause trouble due to colour production, since the coloured substances produced by the addition of chemicals are not easily destroyed by biological means. Experiments have also indicated that sewage-gas liquor mixtures treated with chemicals are not quite so readily oxidized in bacteria beds or in the activated sludge process as chemically treated sewage alone. The difference caused by gas liquor appears to be greater when chemical treatment is employed than when purely biological methods of purification are used.

It may therefore be concluded that, owing mainly to colour production and partly to increased difficulty of biological treatment, processes of chemical treatment would not be so suitable for sewage containing gas works liquor as for sewage alone. Expressed in another way, the effect of gas works liquors on sewage appears to be greater when the sewage is partially or wholly treated with chemicals than when it is purified by exclusively biological methods.

EFFECT OF GAS WORKS LIQUORS ON THE DEVELOPMENT OF ODOURS IN SEWAGE AND ON ITS TREATMENT WITH CHLORINE

Sewage which is allowed to stand out of contact with air gradually undergoes biochemical changes which result in the production of unpleasant odours. The changes are accompanied by the reduction of sulphur compounds in the sewage, resulting in the production of hydrogen sulphide. Sewage in this state is said to be "septic." Spent liquor in average concentrations does not appear to have any influence on the rate at which sewage becomes septic, but ammoniacal liquor in excess of 0.3 per cent. retards it somewhat.²⁶ This is doubtless due to a mild antiseptic action which is more apparent in the absence than in the presence of air.²⁷

The development of "septicity" in sewage is more rapid at higher temperatures and gives trouble in practice in summer in places where, because of the sewers being long or of low gradient, the sewage takes a long time to arrive at the sewage works. In an increasing number of cases septicity is being reduced by the application to the sewage of small doses of chlorine. The amount used does not sterilize the sewage, but is sufficient to delay anaerobic action. It has been found²⁸ that gas liquors very greatly increase the amount of chlorine required to effect complete sterilization, but have not a great influence on the amount required to prevent septicity. Indeed, the effect of spent liquor is hardly measurable and that of ammoniacal liquor is due almost entirely to its content of hydrogen sulphide, which destroys chlorine before it can exert its antiseptic action.

EFFECT OF GAS WORKS LIQUORS ON COLOUR PRODUCTION IN SEWAGE

It has been previously pointed out that innocuous discoloration is not legally regarded as pollution. Nevertheless the alleged production of colour in sewage due to the presence of gas works liquors has been a frequent occasion of complaint. Colours produced in gas works liquors are due entirely to higher tar acids. The latter are rapidly oxidized by atmospheric oxygen in an alkaline solution and almost invariably produce highly coloured products ranging, according to the nature of the liquor, from blues to red and orange. Ammoniacal liquor does not quickly produce colour, either by itself

or when mixed with sewage, because the sulphide which is present is oxidized before the higher tar acids. Spent liquor from which only the free ammonia has been removed is almost neutral in reaction, but oxidation proceeds fairly rapidly if the liquor is shaken in air either with or without the addition of sewage. Spent liquor from which the whole of the ammonia has been removed by the addition of lime is alkaline and oxidation of the higher tar acids takes place very rapidly, resulting in the production of a deep colour almost as soon as the liquor leaves the still.

After mixing gas liquor with sewage the rate of colour production is usually small, owing to the fact that crude sewage contains little, if any, dissolved oxygen. If, therefore, liquors relatively free from colour are admitted to the sewers, the chance of colour developing is not very great.

It has been previously pointed out that the coloured products of oxidation of higher tar acids are not readily destroyed by biological means and, therefore, once colour has been produced in a gas liquor it is likely to persist in the sewage and also in the purified sewage. If, however, colour is not allowed to develop in the liquor before discharge to the sewers the chances of its developing are reduced, since the products of biological oxidation of higher tar acids are colourless.

CONCLUSIONS

It is now possible from the information given in this section to draw some general conclusions regarding the most desirable constitution of a gas works liquor which is to be treated in admixture with sewage. It is also possible, in many of those cases where the discharge of gas works liquor to the sewers gives rise to complaints, to diagnose the trouble and to indicate in what way improvement can be made.

Free Ammonia

It is clear from the experiments quoted that free ammonia in gas works liquor may slow down the rate of purification of a sewage-liquor mixture by activated sludge and may increase the biochemical oxygen demand of the effluents from both activated sludge plants and bacteria beds. If the discharge of crude liquor produces either of these results, the obvious remedy is to remove the free ammonia and to discharge spent liquor.

Sulphide

One effect of the discharge of a liquor containing sulphide to the sewers is that, if the liquor subsequently comes into contact with an acid liquid, gaseous hydrogen sulphide is evolved, rendering poisonous the atmosphere of the sewers. The possibility of this happening is not great but, in view of the serious results which may ensue, it should always be borne

in mind and the liquor discharged to a sewer which does not carry acid liquids at any time. Apart from this and although the limit of tolerance of sewage purification systems for sulphide is rather low, the normal concentration of this substance should not cause trouble once the sewage has been received at the disposal works.

Fixed Ammonia

The amount of fixed ammonia in a gas works liquor is usually considerably smaller than the amount of free ammonia. Its effect on sewage purification is also less, partly because of its smaller quantity and partly because it has no retarding effect on the activated sludge process and, in many cases, its presence in liquor is of little consequence. Where, however, it is found that gas works spent liquor increases the B.O.D. of the effluent from bacteria beds, the fixed ammonia content will usually be the cause and it is therefore preferable that its concentration should be as low as is reasonably possible.

Phenol

It has not been found that phenol in average proportions has any effect on the quality of the purified effluent, and neither the O/A nor the B.O.D. is increased. It must therefore be concluded that, from the point of view of its subsequent disposal in admixture with sewage, phenol is an unimportant constituent of gas works liquor. It does, however, increase the O/A of a crude sewage and those sewage authorities who assess the strength of sewage from this criterion alone may object to it on this account.

Higher Tar Acids

These increase the O/A of a crude sewage and also, because they are not completely oxidized biologically, that of the effluent. To those authorities who judge the character of the purified sewage from the O/A test the presence of higher tar acids will therefore seem undesirable. It has been shown, however, that those tarry bodies which remain unoxidized do not appreciably increase the B.O.D. of the effluent. Of more significance is the fact that the higher tar acids are responsible for any colour produced by gas liquor in sewage and it is, in consequence, desirable that Gas Undertakings should endeavour to reduce the concentration of these bodies as far as is reasonably possible. A further reason is that higher tar acids are in some quarters held responsible for the occasional production of persistent foam in sewage. This subject has not been dealt with in detail because no precise information is available.

Thiocyanate

There are at least three reasons why it is not desirable to produce gas works liquors containing more than a small quantity of thiocyanate.

- (1) Unless the discharge of the liquor to the sewers is carefully balanced, thiocyanate may not be oxidized in the sewage purification system.
- (2) Any thiocyanate formed converts an equivalent amount of free ammonia into fixed ammonia.
- (3) Among the primary products of the oxidation of thiocyanate by sewage bacteria is ammonia which, again, adds to the strength of the sewage.

Thiosulphate

This is not important except in that its formation converts free ammonia into fixed ammonia. Generally methods of working which reduce the extent of thiocyanate formation also reduce the extent of thiosulphate formation.

VII OTHER METHODS OF DISPOSAL OF GAS WORKS WASTE LIQUORS

Having dealt with the disposal of waste liquors by discharge to sewers, it is proposed in this Section to review other methods of disposal, which may be divided into two classes:

- (1) Disposal by direct discharge to river, sea or into the ground.
- (2) Disposal by evaporation.

DISPOSAL BY DIRECT DISCHARGE TO RIVER, SEA OR INTO GROUND

Generally speaking, these methods of disposal are not satisfactory, although there are Gas Works which have adopted them for long periods without experiencing undue trouble. Disposal by discharge into a hole in the ground, such as a disused well, is particularly dangerous, because the ultimate fate of the liquor is uncertain. It may be gradually dissipated and oxidized; on the other hand it may pollute an underground water supply or some stream. In this case the pollution may not disappear immediately the discharge is stopped, but may continue for long periods owing to a large amount of liquor already in the ground. The Gas Undertaking would presumably be liable for any damage caused by this pollution during the whole of the time it existed.

The danger of discharging a toxic liquid like gas works liquor into a relatively small stream is obvious, but the undesirability of admitting it to a river or to the sea, where an adequate dilution is available, is not at first sight apparent. The following argument might be used in its favour. In cases where it is permissible to discharge sewage without biological treatment, there should be a dilution in the stream of at least 150 times. The volume of sewage from a district is usually about 250 times the volume of gas works liquor from the same district, so that the dilution available for the gas liquor in the stream in such cases will be at least 37,000 times, which is much more than sufficient to ensure absence of toxicity in the mixture. This is perfectly true, but uniform mixing of liquids is not always easy to attain and, even if this degree of dilution is ultimately available, local concentrations of gas liquor may persist for a considerable time and cause damage to fish and other life. If, however, the gas liquor is mixed with sewage before discharging to the stream, it is already diluted about 250 times and the possibility of local toxic concentrations existing is remote. Furthermore, by discharging with sewage, the presence of bacteria capable of dealing with the constituents of gas works liquor is ensured, so that oxidation in the stream rapidly occurs. The desirability of discharging the liquor to the sewers rather than direct to the stream therefore becomes clear.

Isolated cases do exist, however, where, owing to the absence of a sewerage system in the district or for some other reason, direct discharge of gas works liquor to a stream is the only practical means of disposal. In such cases it should be the aim of the Gas Undertaking to prevent, so far as is practicable, the occurrence in the liquor of those constituents which are most toxic to fish and other life. These are phenols, higher tar acids and free ammonia.

A further method of disposal of gas works liquor is to spread it on the surface of land. This method is quite distinct from that consisting of discharging to a hole in the ground and is free from most of the disadvantages of the latter. By spreading it over a very large area the liquor is diluted by the water in the soil and in most cases it undergoes rapid biological oxidation. Also the ammonia, free or fixed, present in the liquor acts as a fertilizer unless it is lost by volatilization. The greatest fertilizing effect is obtained with liquors containing the greatest quantities of ammonia and, from this point of view, the most suitable liquor for this method of disposal is ammoniacal liquor. The fertilizing properties of the latter are discussed in Section IX. It is sufficient to remark here that, when ammoniacal liquor is applied to the soil, the amount of ammonia lost by volatilization is relatively small and that the remainder is effective as a fertilizer. The phenol and higher tar acids in the liquor are rapidly oxidized and the thiocyanate may act as a weed killer but is finally oxidized to ammonium sulphate, thereby adding to the fertilizing properties of the liquor. It is essential, however, that the liquor be applied to the soil out of contact with seeds or growing plants since it has a toxic effect on both seeds and leaves and is therefore best applied in the winter or early spring. The cost of transport and distribution of the liquor over the soil may in many cases be considerable but this will be, in part at least, compensated for by its fertilizing value. For small Works situated near a large area of agricultural land and where it is uneconomical to recover ammonia, this method of disposal of ammoniacal liquor may be worth consideration.

DISPOSAL BY EVAPORATION

If gas works waste liquors are disposed of in their liquid form, it must be either to the sewers, to a stream, to the sea, or into or on to the ground. If they are not disposed of in their liquid form, they must ultimately be evaporated.

In evaporation processes there are three chief requirements:

- (1) A cheap source of heat must be available;
- (2) The gases produced must not be allowed to pollute the atmosphere or attack parts of the plant;
- (3) The residue must be capable of easy disposal.

Of these the first is often difficult to satisfy, although it

may be possible to provide sufficient cheap heat to evaporate a portion of the liquor. For this reason, evaporation methods may often only be convenient to use as an adjunct to other methods of disposal. The possibilities of using the steam produced in, and the residue remaining from, the evaporation should be borne in mind, however, since these may justify the use of a more expensive source of heat.

Evaporation in Producers

A number of Works have succeeded in disposing of a proportion of their waste liquor by evaporating it in gas producers. With this method it is impossible to use the steam produced (in excess of a certain quantity) or to recover the residue so that, if additional heat is used, the process is likely to be expensive. The usual method is to replace with liquor the water which is normally used for cooling the grates of the producers. If no more than this is done the heat cost can be taken as nil, since heat would, in any case, be required to evaporate the water which is replaced by the liquor. In this case the amount of liquor which can be evaporated is strictly limited and varies with the type of producer and the practice at any particular Works. It will usually amount to 10 to 20 gal. per ton of coal carbonized, which is not nearly the whole of the liquor.

In one case which has been reported upon,²⁸ spent liquor was distributed over the bars of a step grate producer and its rate regulated so that the ash-pan remained just dry. In case of accident, arrangements were made to prevent any overflow from the ash-pan from entering the drains. Working in this way it was found that 16 gal. of liquor per ton of coal carbonized were evaporated. The residue from the evaporation, whether the liquor was limed or unlimed, was easily removed with the clinker, there was no objectionable smell in the retort house and no sign of corrosion appeared after a considerable period of working. The regulation of the liquor rate required a certain amount of attention but, generally speaking, the process was satisfactory.

The same arrangement was tried with the ammoniacal liquor from the retort house circulating system. This liquor was used because it contained very little free ammonia and was in consequence not very suitable for distillation when only the free ammonia was removed. Difficulty was experienced with the greater amount of residue, due to ammonium chloride, which was left after evaporation. This accumulated on the producer bars and prevented even distribution of liquor and also, on occasions, blocked the liquor feed pipe. In consequence a smaller amount of liquor was evaporated, greater attention was needed and objectionable smells were noticed in the retort house, due to liquor being deflected from the fire by the deposits..

Although the process has been called "evaporation", the

constituents of the liquor are actually subjected to a much more drastic heat treatment. In particular, the whole of the volatile constituents have to pass through the producer and combustion chambers where the phenol, ammonia, sulphide, and other bodies are burnt. Thus, pollution of the atmosphere, except for a negligibly small quantity of sulphur dioxide, does not occur.

If the amount of liquor evaporated on the producers is no greater than the amount of water usually supplied, no extra heat is required for the process. It would be possible to increase the amount of liquor by feeding it further into the fire, but this would mean that more fuel would have to be consumed in order that the same amount of heat might be available for the retorts. This extra fuel would be a direct charge on the process. The producer gas would also contain more carbon dioxide and steam and its temperature of combustion would be reduced, diminishing the temperature of the retorts. The volume of producer gas would be increased, hence it would pass at a quicker rate along the flues and would require a bigger draught; this, however, would not usually be very important. Also the amount of heat carried away by the waste gases would be greater, especially if there were no waste heat boilers. It is not possible to assess all these effects on the basis of costs, which, in addition, are largely influenced by the cost of fuel and the presence or absence of waste heat boilers. In some cases, however, it may be asserted that the cost of evaporating in this way a quantity of liquor exceeding the quantity of water normally used would amount to £1 per 1,000 gal. This would usually be prohibitive.

It may therefore be concluded that, with care, a certain proportion of spent liquor may be disposed of by destruction on the bars of producers. With more trouble some of the ammoniacal liquor may be treated in the same way. But the disposal of more than this quantity would generally prove too expensive and might interfere with the normal conditions of operation in the retort house.

EVAPORATION AT THE BASE OF CHIMNEY STACKS

A portion or, in some cases, all of the waste liquor may be disposed of by evaporation at the base of chimney stacks. This method has the advantage over disposal in producers in that the evaporation takes place after the heating gases have finally left the retort system and therefore it cannot interfere with the normal conditions in the retort house. At first sight it would appear to have the disadvantage, when dealing with ammoniacal liquor, that some of the constituents of the liquor are not destroyed but simply volatilized and their polluting character transferred from the liquor to the atmosphere. This does not appear to be the case in practice; both the hydrogen sulphide and the free ammonia react with the sul-

phur dioxide in the flue gases, producing solid substances, so that atmospheric pollution is not necessarily increased.

The simplest method of carrying out the evaporation is to spray the liquor into the base of the stack, but this is not recommended owing to the possibility of action on the brick-work and the difficulty of removing deposits. This system may be used, without much trouble, for devil liquor, which leaves no residue on evaporation.

It is far better to evaporate the liquor on a series of trays, so fitted in the base of the chimney that their removal for cleaning purposes is not difficult. The trays should be arranged to conform with the following requirements:

- (i) They should not greatly impede the flow of the gases.
- (ii) They should have ample surface to extract heat from the gases.
- (iii) The liquor should travel by a devious path which should not, however, be easily blocked by deposits. A patented process conforming to these requirements is on the market.²⁹

In considering the amount of liquor which can be thus evaporated the following points must be borne in mind:

- (1) Flue gases which have been passed through waste heat boilers, being at a comparatively low temperature, will not evaporate so much liquor as those which have not.
- (2) Where the working of the plant is entirely dependent on the chimney pull, the cooling of the gases and their increase in volume by the addition of water vapour must not be allowed to diminish the pull below the required value.
- (3) The temperature of the gases leaving the top of the chimney must not be below the dew point, otherwise condensation will take place and the condensed liquid may attack the material of which the stack is constructed.

Because of these limiting factors it may be found desirable to evaporate only a portion of the liquor and to dispose of the remainder by another method. There are two ways of accomplishing partial evaporation, (a) to supply only a portion of the liquor to the trays and evaporate that to dryness, and (b) to supply the whole of the liquor to the trays and only partly evaporate it. It will depend on circumstances which of these two methods is preferable. The former will cause more residue to collect and the trays will require more frequent cleaning. The latter, in the case of ammoniacal liquor, will ensure that the whole of the free ammonia is removed from the liquor, but will result in other polluting bodies, with the exception of phenols, remaining in the effluent in more concentrated form.

Evaporation in Specially Constructed Apparatus

Where sufficient cheap heat such as surplus steam or coke breeze is available it may sometimes be justifiable to dispose of the liquor in a specially constructed evaporator, the resulting gases being suitably treated. In one case where this has been adopted,³⁰ a regulated flow of liquor passes from a settling tank into a preheater fitted with a closed steam cylinder and steam trap. Thence the liquor passes to the evaporator where the liquid falls in drops on to a cylinder heated by closed steam. The resulting concentrated liquid is of sufficient consistency to permit of its being mixed with fuel and burnt. The vapours from the preheater and evaporator are passed to boiler flues.

A far more ambitious method, which is in operation on the large scale, has also been patented.³¹ In this process the liquor is evaporated by heat specially generated for the purpose, high pressure steam being favoured, the justification for the special generation of heat being (a) that the steam produced in the evaporation can be used for purposes for which pure steam is unnecessary and (b) that from the residual concentrated liquor ammonium chloride, which is a saleable product, can be crystallized. The impure steam can be used for such purposes as the steaming of retorts, the supply to producers, the generation of water gas and the distillation of ammoniacal liquor. Either ammoniacal liquor or liquor which has been stripped of its free ammonia can be evaporated but, in the case of the former, the last mentioned outlet for the steam produced would, of course, be no longer available. The ammonium chloride produced would be impure, the amount of impurity depending mainly on the higher tar acid and thiocyanate content of the liquor. In the patents, the treatment of the vapours leaving the liquor for the recovery of phenols is included and in certain circumstances this would be an economic proposition. Although a large-scale plant is in operation, the economics of the process depend so much on local conditions, such as the composition and volume of the liquor, the possibilities of use of the steam produced and the market for ammonium chloride, that they cannot well be dealt with here. Allowance must, however, be made on the credit side for the fact that the whole of the liquor is completely disposed of without nuisance and within the Works.

Use of Gas Works Liquor in the Quenching of Coke

One method of evaporation of liquor which has been more extensively adopted by coke ovens than by Gas Works is to use it for the quenching of coke. It has been stated³² that coke quenched with ammoniacal liquor is generally not distinguishable in properties from that quenched with water. It was also stated that no smell of ammonia or hydrogen

sulphide was produced and that the only noticeable smell was a slight phenolic one which was not unpleasant. No corrosion of the structural work in the quenching tower had been noticed after nine months' working. It is obvious why this method has not been more largely used on Gas Works: coke from vertical retorts requires very little quenching; coke from horizontal retorts is usually quenched in the retort house itself and any odours produced would be very noticeable; and Gas Works, in contrast to many coke oven installations, are usually situated near to centres of population, the inhabitants of which would be likely to complain of odours. The method might, however, be used in special circumstances.

Other Evaporation Methods

Other processes which involve the partial evaporation of the liquor are in use but these may be classed as methods of improving the liquor for subsequent treatment or disposal by other means and are therefore more properly dealt with in the next Section.

VIII METHODS FOR IMPROVEMENT IN LIQUOR PRODUCTION AT GAS WORKS

Whatever method of disposal of waste liquor is adopted by a Gas Undertaking, it is obvious that the liquor should be made as suitable as possible for that method of disposal. In general there are three methods by which this can be done:

1. The volume of liquor can be reduced as much as possible. Obviously, other things being equal, the smaller the quantity of liquor for disposal the more easily this is effected. It should be borne in mind, however, that disposal is not always facilitated if the reduction in volume is accompanied by a corresponding increase in the concentration of all the constituents.
2. The process of gas making can be so arranged that those constituents which cause most difficulty in the method of disposal adopted are absent from, or present only in small quantities in, the ammoniacal liquor. But it must be remembered that in gas making other factors are more important than the production of a good liquor.
3. After the liquor has been produced, it may be specially treated for the removal of a constituent or constituents which cause difficulty in disposal. For example, it may be distilled to remove ammonia, sulphide, etc., although the primary object of such treatment is not usually to improve the composition of the waste liquor.

METHODS OF REDUCING THE VOLUME OF WASTE LIQUOR

A considerable reduction in the amount of gas works liquor produced is not always easy to accomplish. It is impossible to avoid, for instance, the production of water from the decomposition of the coal carbonized. Also, it is usually not practicable to dry the coal before carbonization. The "water of constitution" of the coal and its moisture content must therefore always reappear in the liquor produced, so that the volume of this must usually be at least 20 to 30 gal. per ton of coal carbonized.

The volume of liquor will be increased by any steam supplied as such to the retorts and not decomposed therein. If the charge is steamed to the extent of 15 per cent. of its weight and only 60 per cent. of the steam is decomposed, the remainder will reappear in the liquor and increase its volume by 13.5 gal. per ton of coal carbonized. Steaming is usual with continuous vertical retorts, but is not generally practised where horizontal retort systems are used, although it is being adopted in some cases. With horizontal retorts, the percentage of steam decomposed is usually relatively small, the amount of steam required to produce a given quantity of water gas is large and, for both these reasons, the amount of steam reappearing in the liquor is also large. The result is a liquor

weak in ammonia, which renders ammonia recovery more expensive, and large in volume, which may increase the difficulties of disposal. Whatever may be the merits of steaming horizontal retorts from a gas making point of view, from the standpoint of ammonia recovery and waste liquor disposal it is definitely bad practice.

The volume of the liquor is also increased by any water used for removing tar fog from the gas and for scrubbing it free from ammonia. This is generally of the order of 10 gal. per ton of coal carbonized.

Assuming it to be impracticable to reduce the moisture content of the coal and its water of constitution, and undesirable, for other reasons, to reduce the amount of steaming and the proportion of undecomposed steam, it is evident that the only direct way of reducing the volume of liquor produced is to reduce the amount of fresh water used for scrubbing purposes. This can be accomplished by adopting one or other of the following methods:

- (i) The efficiency of the scrubbing system can be made as great as possible, thus reducing the amount of scrubbing medium necessary. This can be done by suitable choice of scrubbers, by operating these in the best possible way and by securing that both gas and water entering the scrubber are as cool as possible.
- (ii) The fresh water used in the scrubbers may be replaced by part of the spent liquor. By this means, the amount of waste liquor for disposal is decreased but it does not follow that its polluting character will be decreased, since the spent liquor used in the scrubbers will pick up additional quantities of thiosulphate and thiocyanate. The spent liquor should be effectively cooled before use and supplied to the scrubbers at a slightly greater rate than the fresh water which it replaces. Spent liquor from which the fixed ammonia has been removed by the addition of lime is unsuitable for use in the scrubbers, since the carbon dioxide in the gas will convert the calcium salts in the liquor into calcium carbonate, the deposition of which will cause incrustations to form.
- (iii) Part or, in some cases, all of the fresh water used in the scrubbers may be replaced by a liquor, weak in ammonia, which has previously condensed from the gas. It has been pointed out (p. 7) that the liquor produced in the condensers of a gas making system is generally weaker in free ammonia than that which has been used in the scrubbers. It follows that condenser liquor could be used in the scrubbers to remove from the crude gas a portion at least of its residual ammonia, with consequent saving in fresh water required

in the last stages of scrubbing. It is possible, however, to do more than this by taking advantage of the fact that liquors condensing in different parts of the condenser are not all of the same strength; the higher the temperature of condensation the weaker the liquor. H. Hollings,³³ considering data respecting the equilibrium between gas and liquor, shows that "if it is permissible to allow a maximum of (say) 5 gr. of ammonia per 100 cu.ft. of gas to pass forward from the ammonia washing system to the oxide of iron purification system . . . , it would be possible to recover the rest of the ammonia from the gas without the introduction of fresh water for washing, provided that the temperature is kept reasonably low and provided that a washing liquor containing no more free ammonia than the equivalent of about 1.5 oz. strength could be procured from some other part of the system." Hollings proceeds to show that this can be done by making use of the weak liquor condensing in the first part of the condensers and describes an arrangement which operates successfully.

Such a process is intended primarily for use with vertical retort gas containing at least 3.5 per cent. of carbon dioxide. The primary condensate from horizontal retort gas of much lower carbon dioxide content will itself contain less carbon dioxide and, in consequence, its partial pressure of ammonia will be greater. If this condensate were used for scrubbing the gas, the amount of ammonia slip would be too great unless fresh water were used at a later stage. This difficulty can be overcome by allowing the liquor to absorb carbon dioxide from a suitable source before its use as a scrubbing medium.³⁴

It will be appreciated that the successful use of any such system depends largely upon the condensing and washing systems being efficient. The result of its adoption is a decreased volume of waste liquor for disposal and also, a matter which will probably be considered more important, the production of an ammoniacal liquor much richer in ammonia and more economical to distil.

Partial Evaporation for the Improvement of the Liquor

It is proposed to consider here processes which involve the evaporation of part of the liquor, the purpose of the evaporation being to improve the residual liquor from the point of view of ammonia recovery and effluent disposal. It is impossible to make a complete distinction, however, between these processes and those previously dealt with (p. 58), where the sole aim of evaporation was finally to dispose of some or all of the waste liquor.

Partial Evaporation for the Recovery of Ammonium Chloride

A process in which spent liquor is evaporated and ammonium chloride is recovered from the residue has already been described (p. 62). It is possible, however, to recover a considerable proportion of the ammonium chloride in the liquor by evaporating only a small portion of it, this portion being suitably chosen. The recovery of ammonium chloride as such not only produces a saleable product but (a) if the fixed ammonia is normally recovered as sulphate, it results in a saving in lime and sulphuric acid, or (b) if fixed ammonia is not recovered, it reduces the total ammonia content of the liquor ultimately disposed of. Having regard to the importance of the ammonia content of liquor where it is disposed of in admixture with sewage, the preliminary removal of a portion of the fixed ammonia may be a considerable advantage. In addition, the liquor which is evaporated for the recovery of ammonium chloride is that which has had the greatest amount of contact with tar and is therefore rich in higher tar acids. Hence some of these colour producing substances are prevented from entering the sewers. A further point is that the liquor which is evaporated is very weak in free ammonia and, unless fixed ammonia is recovered, may not be worth distillation.

It is usual to circulate liquor through hydraulic mains. This assists in keeping the mains free from blockages and also, if high pressure sprays are used, separates a good deal of tar from the gas. All substances of low volatility tend to condense in the early stages and among them is ammonium chloride, which dissolves in the circulating liquor. If, now, the circulating liquor is re-circulated without intermediate cooling, little or no condensation of liquor from the gas will take place in the hydraulic main but ammonium chloride will continue to dissolve in the circulated liquor, which will therefore become more concentrated with respect to this substance. By continuing the process over a long period a liquor can be obtained which contains more than 20 per cent. of ammonium chloride. This liquor is removed from the system and evaporated, not to dryness but to such a stage that on cooling it deposits most of its ammonium chloride in crystalline form. The crystals are separated from the mother liquor, which is put back into circulation. The ammonium chloride should be of over 99 per cent. purity, but usually becomes dark coloured on exposure to light and air. This can be prevented by recrystallization or treatment with organic solvents such as pyridine or tri-cresyl-phosphate.

Such a process is often worked at coke ovens, but rarely at Gas Works. It is cheap to operate in comparison with the value of the product but it needs a certain amount of attention. A disadvantage is that the tar which separates in

the hydraulic main and comes into contact with a liquor high in chloride content is itself likely to be contaminated with chloride.

*Partial Evaporation Using the Sensible Heat
of the Crude Gas*

Theoretically, there is more than sufficient heat in the steam-laden crude gas leaving the retorts to evaporate the whole of the liquor produced by condensation from the gas. It is not easy, however, to make this heat available for the purpose. One process which has been patented³⁵ accomplishes the evaporation of 30 to 40 per cent. of the total liquor, although in doing so some 10 to 15 per cent. of the total ammonia is sacrificed. The principle of the method is briefly as follows:

Hot coal gas leaving the hydraulic main is caused to flow through a washer where it is washed with a concentrated solution of a salt. In practice this solution is one of ammonium chloride obtained from the gas itself by recirculation of hot liquor through the hydraulic main in the manner previously described. The temperature of the solution should be just above the dew point of the gas but, owing to the presence of salts, its vapour pressure is lower than that of water at the same temperature. Hence, in spite of its high temperature, water is extracted from the gas by this liquor but, because of its high temperature, the amount of ammonia extracted is small. The gas leaving the washer now contains much less water than before but not much less ammonia and, therefore, a much stronger ammonia solution is obtained on cooling and washing. The concentrated solution of ammonium chloride as it leaves the gas is considerably hotter and also rather more dilute than before and, by some arrangement such as allowing the liquor to flow over evaporating racks, this extra heat is used in partially evaporating the liquor and restoring its original concentration. In this process a slight amount of ammonia is lost to the atmosphere. Presumably if and when the concentration of ammonium chloride in the circulating liquor becomes too great, a portion would either be evaporated to recover the salt or simply mixed with condenser liquor.

This process would be of greatest use to Undertakings willing to sacrifice a small portion of the ammonia in order to reduce the volume of liquor considerably, *e.g.*, to Undertakings which have to pay for transport of crude liquor and to those which are strictly limited as to the amount of effluent they may discharge to the sewers. In some cases, it may be worth while sacrificing a little ammonia in order to produce a stronger liquor and one which is therefore cheaper per unit of ammonia to distil. Another advantage is that the liquor

which is evaporated is precisely that which is most contaminated with higher tar acids and, therefore, which contributes most to the increased oxygen absorption of a sewage effluent and to colour production. In addition, if the circulating liquor is never allowed to mix with the condenser and scrubber liquors, these should contain little fixed ammonia which is a further advantage. The process, however, requires a certain amount of chemical control and, unless care is taken, the evaporation may result in the production of odours due to phenols and ammonia.

Partial Evaporation into the Base of Continuous Vertical Retorts

If it be granted that the ammonia in ammoniacal liquor is of no value then it may, in certain circumstances, be justifiable to destroy it by distilling into the base of continuous vertical retorts. Such a process has been described.³⁶ The liquor, preheated if possible, is pumped through sprays into the coke boxes at the base of the retorts. In cooling the coke, the liquor is heated and some ammonia and steam pass upwards through the retort. The hot liquor then passes to an ordinary free ammonia still heated by exhaust steam. Distillation is here completed and the distillation gases, including ammonia, steam, carbon dioxide, hydrogen sulphide and some phenols, pass direct to the retorts. Here the ammonia is cracked, producing nitrogen and hydrogen, and the phenols are also decomposed; some of the steam and carbon dioxide react with the coke; but the fate of the hydrogen sulphide has not been determined. The spent liquor from the still should be rather smaller in volume than usual and contain less phenols; it is disposed of by any recognized method.

Detailed comment on this process is unnecessary. It works satisfactorily and may appeal to Undertakings where ammonia cannot be recovered except at a loss and where, at the same time, it is impossible to dispose of the ammoniacal liquor as such. In these cases, there seems no reason why the steam usually supplied to the vertical retorts should not be replaced by the distillation gases from an ammonia still. At first sight, this replacement may appear advantageous because of the thermal value of cracked ammonia ($N_2 + 3H_2$), but the fact that the calorific value both of this gas and of the mixture of CO_2 and CO produced by the action of the CO_2 on the coke is less than that of water gas is at least an equivalent disadvantage.

METHODS OF IMPROVING THE COMPOSITION OF GAS WORKS LIQUOR DURING ITS PRODUCTION

It was pointed out in Section I that the composition of an ammoniacal liquor and, therefore, of the corresponding spent liquor, is greatly influenced by conditions of carboniza-

tion, condensation and scrubbing. Carbonization in horizontal retorts, for instance, results in the formation of liquors containing only small quantities of higher tar acids and such liquors are, in consequence, more easily disposed of in admixture with sewage in those cases where colour production is likely to be troublesome and where it is inadvisable that the oxygen absorption of the purified sewage should be increased. It is always desirable that the higher tar acid content of a liquor should be as low as possible, although there may be more pressing reasons for this in some cases than in others. Methods of reducing the higher tar acid content of a liquor will therefore first be examined. These will apply mainly to vertical retort liquors, since such liquors, unless care is taken, contain large quantities of these colour-producing bodies.

Methods of Reducing the Higher Tar Acid Content of Liquors

Higher tar acids, in contrast to monohydric phenols, are not volatile in steam; normally, therefore, they condense with the tar and not with the liquor. If, however, tar and liquor condense at the same time or if they are subsequently brought into intimate contact with each other, higher tar acids are transferred from tar to liquor until equilibrium is reached. In order to avoid this transference it is necessary to prevent contact occurring.

Tar and liquor are normally brought into contact with each other at the following stages:

- (i) In the retort house liquor circulating system. This cannot well be avoided, if liquor is circulated at all, but its effect can be minimized. Many Works produce, in the condensers and scrubbers, a liquor relatively free from higher tar acids, but allow this liquor to flow to a storage well from which liquor is pumped to the circulating system. By this means the liquor becomes grossly contaminated with higher tar acids and is made less suitable for disposal. It is far better to have a small storage well specially for circulating liquor and to pump from and deliver into this well, only allowing the overflow, if any, to flow into the main storage tank. By this means not only can higher tar acids be prevented from contaminating the bulk of the liquor but the circulating liquor can be worked up for the recovery of ammonium chloride, the advantages of which have already been mentioned.
- (ii) In the condensers and scrubbers. This can be avoided by ensuring that tar separation is complete before liquor begins to condense. This problem, therefore, resolves itself into the adoption of efficient tar separators acting on the hot crude gas.

- (iii) During storage, if tar and liquor are stored in the same well. This can be avoided by having separate storage wells for tar and liquor.

Tar Separation from Hot Crude Coal Gas

Tests on several methods of tar separation from the hot gas have been made by the Liquor Effluents and Ammonia Committee. One of the separators³⁷ consisted of a restricted gas main in which a finely divided spray of liquor at 50 lb. per sq.in. impinged on the gas stream. By this means, the volume of tar deposited in the retort house was increased from 4.7 to 11.6 gal. per ton of coal and the higher tar acid content of the liquor condensing subsequently was reduced by approximately 25 per cent. At another Works, the effect of a cyclone tar precipitator was studied.³⁸ It was found that the effective operation of this, together with the adoption of a closed liquor circulating system, lowered the higher tar acid content of the stock liquor by more than 50 per cent. By far the most efficient tar precipitator, however, was found to be an electrostatic detarrer,³⁹ which virtually removes 100 per cent. of the tar fog from the gas. Its effect on the composition of the ammoniacal liquor is recorded in Table 15.

TABLE 15.—*Influence of Electrostatic Detarrer on the Composition of Ammoniacal Liquor*

—	Without Tar Precipitator.	With Tar Precipitator.
1	2	3
Higher tar acids, O ₂ absorbed in aeration test, g. per 100,000	94	11
"Difference" figure of oxygen absorption, pts. per 100,000	408	113
Phenols, g. per 100 c.c.	0.403	0.742
Total oxygen absorption (4 hr. 27° C.), pts. per 100,000	1,191	1,450

Assessed on the basis of the aeration test, the reduction in the higher tar acid content of the liquor effected by the detarrer was 88 per cent.; on the basis of the difference figure it was 72 per cent. It was also noted that the liquor produced with the detarrer in operation, when made alkaline and a 1 per cent. solution in water shaken with air, gave a very slight colour compared with liquor produced without the detarrer in operation and treated similarly.

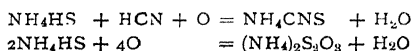
It will be seen from the above analysis that one effect of the detarrer was greatly to increase the phenol content of the liquor, so that, although the higher tar acid content was diminished, the total oxygen absorption was increased. Phenol is volatile in steam, the ratio of phenol to water in the vapour phase being about twice the ratio in the liquid phase.

Hence there is some tendency for the phenols to condense with the liquor rather than with the tar. When the tar is not completely separated from the hot gas, this tendency is counteracted by the transference of phenols from liquor to tar as these condense together. This cannot take place where tar is completely separated from the hot gas and the phenol concentration in the liquor is therefore larger.

In the particular case under consideration (Table 15), the increase in oxygen absorption due to the phenols, as a result of the action of the detarrer, was greater than the decrease due to higher tar acids, the net result being a liquor of higher O/A. Judging by this determination alone, it appears that the use of the detarrer resulted in the production of a liquor less suitable for disposal by way of the sewers. The converse in fact obtains, since phenols are easily and completely oxidized biologically, whereas higher tar acids are not completely oxidized and, in addition, are likely to produce coloured effluents. It will also become apparent later that a liquor such as is produced with the detarrer in operation is eminently suitable for treatment in phenol recovery plants, since the high phenol content ensures a greater yield of product and the low higher tar acid content increases the purity of the product.

Methods of Reducing the Thiocyanate and Thiosulphate Content of Liquors

Both thiosulphate and thiocyanate are oxidation products of sulphide:



The extent to which both these reactions take place during liquor production is governed by (1) the oxygen content of the liquor (which in turn is controlled by the oxygen content of the crude gas), (2) the time of contact between gas and liquor (since the reactions take place relatively slowly), and (3) the sulphide content of the liquor. In addition, the production of thiocyanate depends on (4) the cyanide content of the liquor.

- (1) Unless the retorts are leaking badly and are worked under a slight vacuum, the crude coal gas leaving them should contain little or no oxygen. It is customary, however, to add a little oxygen to assist the oxide of iron purification process. This is often done by allowing a small quantity of air to be pulled in to the gas stream at the exhausters. In this case the gas contains oxygen while it is passing through the washers and scrubbers, and the oxidation reactions producing thiosulphate and thiocyanate are facilitated. In order to minimize the production of

these substances air for purification purposes should be admitted not at the exhausters but at the inlet to the purifiers. This is now done at a number of Works, which use special small blowers for the purpose.

- (2) The time of contact between gas and liquor in the ammonia scrubbers varies considerably. In particular, it is very much greater with tower scrubbers than with rotary scrubbers and it has been found that tower scrubbers usually yield a liquor of high thiocyanate and thiosulphate content. In order to reduce the production of these compounds, it is desirable that the time of contact of liquor and gas should be the minimum necessary to remove ammonia.
- (3) It is not easy to control the sulphide content of a liquor. It is worthy of note, however, that, where the semi-direct process of ammonia recovery is employed and the ammonia scrubbers are replaced by secondary condensers where cooling is by indirect contact, little or no sulphide is removed from the gas. In these circumstances the production of thiocyanate and thiosulphate is exceedingly small.
- (4) The cyanide content of the crude gas depends to some extent on the system and temperature of carbonization, but it has not been observed that variations due to this cause are sufficient to influence appreciably the amount of thiocyanate produced. Cyanide can, however, be largely removed from the gas in a cyanide washer (where it is usually converted into thiocyanate and sold as such) and, if this is done, the subsequent production of thiocyanate should be greatly diminished.

It is not possible to give figures to show the effect of these factors individually on thiocyanate and thiosulphate production but the total effect can be gauged from the fact that the thiocyanate content of liquors has been found to vary from 0.05 g. per 100 c.c. under the best conditions to 1.5 g. per 100 c.c. under the worst.

METHODS OF TREATMENT OF GAS WORKS LIQUORS AFTER THEY HAVE BEEN PRODUCED

The third possible way in which gas works liquors can be made more suitable for disposal is to treat the liquors, after they have been produced, for the removal of certain compounds the presence of which makes them less suitable for the particular method of disposal adopted. Among such methods may be included the removal of ammonia, since, although this is usually undertaken primarily as a commercial proposition for the recovery of the ammonia, its effect on the

nature of the liquor is profound and, more than any other process of treatment, it facilitates the disposal of the liquor by the most commonly used method, *i.e.*, discharge to the sewers. The subject of ammonia recovery is, however, a large one and is dealt with in some detail later.

Other processes to which liquor may be subjected with the object of facilitating disposal are treatment for the removal of phenols and biological oxidation at the Gas Works. Several other processes have been suggested but none appears to have sufficient attraction to justify its employment on a large scale.

Phenol Recovery

A large number of patents for the removal of phenols from liquor produced in the carbonization of coal have been granted in this and other countries and, at a number of places, particularly abroad, phenol recovery is practised. This requires some explanation in view of the conclusion on page 55 that, from the point of view of its subsequent disposal in admixture with sewage, phenol is an unimportant constituent of gas works liquor. The great majority of phenol recovery plants operate on liquors from coke ovens. These liquors differ from an average gas works liquor in that they contain smaller quantities of higher tar acids and, if the direct or semi-direct process of ammonia recovery is employed, only small quantities of thiosulphate and thiocyanate. Their chief polluting constituent is therefore phenol and, if purification is necessary, phenol is the only constituent it is practicable to remove. Since, particularly in Germany, waste coke oven liquor is not usually disposed of in admixture with sewage but is discharged direct to a river, the fact that phenol readily responds to treatment in admixture with sewage is in these circumstances of no importance.

Processes for phenol recovery may be divided into three classes according to whether the reagent used for the extraction is solid, liquid or gas. The only solid absorbent which has been used is active carbon; of the liquid solvents, benzole has proved the most popular, but tri-cresyl phosphate and tar oil have also been employed; gases used for the extraction have been hot air, flue gases and steam.

Phenol Recovery Processes Using Liquid Solvents

A solvent for the recovery of phenol from gas works liquor should satisfy the following requirements:

- (a) It should have a considerable solvent power for phenols.
- (b) It should itself be almost insoluble in liquor.
- (c) It should have a density sufficiently far removed from that of the liquor to allow of separation by gravity.
- (d) Phenols should be easily recovered from it.
- (e) Solvent losses should be replaceable at small cost.

Benzole satisfies most of these requirements.

A number of phenol recovery plants using benzole have been described⁴⁰ and factors influencing the efficiency of the process studied.⁴¹ Different plants vary in detail of construction and method of operation, but the general principles can be briefly described. The ammoniacal liquor is first freed from tar particles by passing through some kind of filter and then, after heating to about 60° C., at which temperature washing is both more rapid and more complete, is led to the top of the phenol washer. This is a tall vertical column and liquor enters at the top and benzole at the bottom. The washer contains some arrangement for ensuring intimate contact between the two liquids, being either packed with rings or fitted with a series of sieve trays through which the liquor has to pass on its way down the washer. Although intimate contact should be aimed at, it is not desirable that the liquids should be split up into too small droplets, since this would cause loss of benzole by entrainment in the liquor. The liquor leaving the washer contains some benzole (about 0.15 g. per litre) in solution and it is essential, for economical working, that this should not be lost. In coke ovens using the semi-direct process of ammonia recovery this benzole is removed from the liquor during the distillation and is conveyed into the stream of coke oven gas, from which it is recovered in the benzole recovery plant. Another method of recovering the dissolved benzole is to pass the liquor through active carbon, which retains the benzole and from which benzole is recovered by steaming.⁴² The efficiency of phenol removal from the liquor varies from 80 to 95 per cent. and at the same time a small proportion of the higher tar acids is removed. After use, the benzole is treated for the recovery of phenol, for which there are two chief methods, (i) distillation and (ii) extraction with caustic soda. In the first method the benzole is distilled off and the residue, which contains about 70 per cent. of phenols, is sold. In this method it is obviously desirable to keep the amount of benzole used for washing as small as possible, consistent with efficient washing. In the second method the benzole is washed with a solution of caustic soda for the extraction of phenols and these are recovered from the resulting sodium phenolate solution by acidifying with sulphuric acid, carbon dioxide or some weakly acid salt such as sodium bicarbonate. In Germany it was found that this second method was generally cheaper to use.

The economics of the process are controlled mainly by (a) the phenol content of the ammoniacal liquor, (b) the amount of benzole lost in the process and (c) the value of the phenols recovered. The cost of treatment per given volume of liquor is almost independent of the concentration of phenol in the liquor and therefore the greater this is the greater the chance of the process proving economical. With prices at their present level, it is probable that phenol recovery from a

liquor containing 0.3 g. phenol per 100 c.c. would pay. With a liquor much richer in phenols, such as is obtained by the use of an electrostatic detarrer on the hot gas, phenol recovery should show a fair profit, particularly as the quality of the product would be improved owing to the absence of higher tar acids.

It has also been proposed to use tri-cresyl phosphate, a heavy liquid of high boiling point, as a solvent for the recovery of phenols⁴³ and at least one large scale plant using this substance has been in operation. The advantages are (i) that tri-cresyl phosphate is very much less soluble in liquor than is benzole and therefore losses of solvent are much reduced, (ii) owing to its great solvent power for phenols it is necessary to use only a very small amount of it for the extraction and the concentration of phenols in the used solvent is high and (iii) because of its high boiling point the phenols may be recovered from it by distillation at a low cost and in a much purer form. The disadvantages are its high cost and a tendency for it to deteriorate on continued use. The process does not appear to have made much headway.

Dephenolated tar oils have also been suggested for use as a solvent for phenols. They have the advantages over benzole of lower volatility and solubility in liquor, but the difficulties attendant on their production and use have not been overcome.

Phenol Recovery Using Active Carbon

When ammoniacal liquor is passed through active carbon a large proportion of the phenolic constituents is retained by the carbon. A plant embodying this principle for phenol recovery has been described.⁴⁴ The liquor, after removal of suspended tar particles and preheating, is passed through one of two absorbers filled with active carbon of suitable type and particle size. This removes the phenol until the "break point" is reached, when the liquor is diverted into the second absorber. Preheated benzole is then passed through the first absorber to remove the phenol and the phenol finally separated from the benzole by distillation. The last traces of benzole are removed from the carbon by steam and the absorber is again ready for use. It has been claimed for this process that it gives a higher efficiency of phenol removal from the liquor, that benzole losses are small and that operating costs are low. It has not, however, proved as popular as the benzole washing process.

Phenol Recovery by the Use of Hot Gases

As has been stated the hot gases which have usually been suggested for this purpose have been steam or a mixture of steam and air, but the use of vapours of such substances as trichlorethylene has also been patented.⁴⁵ The first large-

scale plant using air and steam has been described.⁴⁶ The liquor treated is that leaving the section of the ammonia still which removes the free ammonia. This is pumped to the top of a tower packed with suitable material up which a mixture of 90 per cent. steam and 10 per cent. air is blown. This removes the phenol from the liquor and an efficiency of 95 per cent. is claimed. The phenol laden air-steam mixture is then passed up a tower down which a concentrated solution of caustic soda flows and here the phenol is extracted, forming sodium phenolate, and the gases are then repassed to the first tower. Thus the gases are continually in circulation, phenol being recovered from the caustic soda solution on acidulating by any convenient method. Since both liquor and soda solution are kept near boiling point and the towers are effectively lagged there is little heat loss in the process and the only considerable cost is that of pumping liquor and blowing the gas mixture. The process might be made more efficient by operating under pressure.⁴⁷

It has also been claimed that phenol can be economically removed from liquor by simple distillation with live steam⁴⁸, but investigation⁴⁹ did not support this claim.

Bacterial Purification of Gas Liquors at the Gas Works

It has been shown in Section VI that gas works liquors are amenable to biological oxidation when mixed with a large volume of sewage. Attempts have been made to accomplish the same work at the Gas Works with the aid of only a small quantity of sewage. One such plant has been investigated in some detail.⁵⁰ It consisted of bacteria beds which were matured by first treating domestic sewage on them. Small quantities of spent liquor were then added to the sewage and the proportion was gradually increased until more liquor than sewage was supplied to the plant. This mixture was diluted with a large proportion of the effluent from the plant before being fed to the beds. There was thus a recirculation system from which a small proportion of the effluent was continually led off and discharged to the sewers and to which a small proportion of spent liquor and sewage was continually added. A considerable proportion of the organic matter in spent liquor was oxidized in the process but, when ammoniacal liquor was treated in the same way, there was very little oxidation. The process was expensive in both capital and running costs and has now been abandoned at this particular Works. It is considered that biological treatment is best and most efficiently carried out at a Works specially designed for it and where the dilution available for the liquor is very large, *i.e.*, a sewage treatment works. It is, indeed, doubtful if the adoption of bacterial treatment at a Gas Works does materially lessen the burden on a sewage works. The only constituents oxidized in a Gas Works plant are phenols and

some of the higher tar acids and thiocyanate. Those substances, including any ammonia, free or fixed, which are difficult to oxidize biologically and which tend to reduce the quality of the purified sewage, are not oxidized in a Gas Works plant and, therefore, even if the amount of purification, on an O/A basis, effected by the prior bacterial treatment is large it does not mean that the load on a sewage works is proportionately reduced.

IX THE FERTILIZING PROPERTIES OF GAS WORKS AMMONIA PRODUCTS

In the past it has been the almost universal practice for ammonia to be recovered as ammonium sulphate which has found its chief commercial use as a fertilizer. Owing to the high price of sulphate of ammonia which ruled until after the Great War, its production and sale yielded a considerable amount of revenue to Gas Undertakings. With the advent of sulphate prepared from synthetic ammonia, however, prices slumped and reached as little as £5 5s. per ton in 1932. At this figure, most Gas Undertakings found that the production of sulphate did not pay and attention was therefore directed towards the cheapening of ammonia recovery either by (i) economies in sulphate manufacture by existing processes, or (ii) the adoption of new processes for the production of sulphate or (iii) the recovery of ammonia in some other form. The last suggestion was attractive since the chief item in the cost of sulphate manufacture was the relatively high cost of sulphuric acid. The use of this substance might be avoided if some other salt could be manufactured.

The commercial success of any process for the recovery of ammonia in a form other than sulphate depends not only on the technical aspect but on whether a suitable market can be found for the product. It should be borne in mind that the quantity of ammoniacal liquor produced at Gas Works in Great Britain is equivalent to about 150,000 tons of ammonium sulphate per annum, so that before any change can be made in the form in which the ammonia is recovered some market must be available for large quantities of the new product. The great bulk of the ammonium sulphate which is at present produced is used either directly or indirectly as a fertilizer and it does not appear, at the present time, that there is any other market which could absorb such large quantities of ammonium salts. There may be special circumstances in which a particular Undertaking may find it advantageous to make a relatively small quantity of some ammonia product and to develop a specialized business but, in general, it may be assumed that it would not be a commercial proposition to manufacture any ammonium product unless that product could be used efficiently as a fertilizer. It is therefore essential that the fertilizing properties of alternative ammonium products should be compared with those of sulphate.

FERTILIZING ACTION OF AMMONIUM COMPOUNDS

Growing plants require nitrogen for the synthesis of protein matter which is one of their essential constituents. Most classes of plants derive their nitrogen entirely from the soil and nitrogen is most easily assimilated by them when it is present as the nitrate ion. It is not necessary, however, for

nitrogen to be applied to the soil in this form since organisms normally occurring in soil can convert ammonium salts and organic nitrogen compounds into nitrate by oxidation processes. Thus, the fertilizing action of farmyard manure, as regards nitrogen, is dependent on the hydrolysis of proteins and other organic nitrogen compounds to ammonia, followed by the oxidation of ammonia to nitrate and the absorption of nitrate by the plants. The most common form of nitrogenous artificial fertilizer is ammonium sulphate, although a considerable quantity of sodium nitrate is also used and "concentrated fertilizers" containing, in addition to nitrogen, other plant foods such as compounds of potassium and phosphorus are becoming increasingly popular.

When an ammonium salt is added to an arable soil, the ammonium ion exchanges with the exchangeable bases in the soil and remains in intimate association with the soil until it is converted into nitrate by the soil micro-organisms. This process normally takes place in a few days or weeks. After nitrification of the ammonia has taken place, the only differences which can exist between different forms of nitrogenous fertilizers must be due to constituents of the fertilizer other than ammonia, *i.e.*, in the case of ammonium salts, to the anion of the salt. Before nitrification takes place ammonium compounds may show differences due to some specific properties of the compounds; some compounds may be toxic to growing plants, some may lose ammonia rapidly from the soil before absorption takes place and some may undergo reactions which may deplete the soil of an essential constituent, etc. These are the possibilities to which the greatest attention must be paid when comparing the fertilizing properties of different ammonium compounds and their study is facilitated because, in the main, any differences will become apparent soon after the fertilizer is applied to the soil.

Ammonium Sulphate

The fertilizing properties of ammonium sulphate have been studied for very many years but, even now, the mechanism of the reaction which takes place between the fertilizer and the soil is not fully understood. It is certain, however, that calcium is lost from the soil after the application of ammonium sulphate. This loss is explained by the action of the sulphuric acid, which is liberated when the ammonium ion enters the soil particles, on the calcium carbonate present in the soil or, if this is absent, on the calcium contained in the soil particles. Thus the continued use of ammonium sulphate eventually leads to soil acidity which must be counteracted by the further addition of lime or calcium carbonate if the soil is to remain in good condition. The amount of calcium carbonate removed from the soil is about equal to the amount of sulphate applied. This must be reckoned as a disad-

vantage attending the use of sulphate. The sulphate radical has itself nutrient value for certain plants and has no harmful physical effect on the soil, but it must be regarded primarily as a carrier for the ammonia.

Nothing need be said concerning the effect of ammonium sulphate on the yield of crops, since it is widely known that this is generally considerably increased. The extent of the increase serves as a useful standard with which the performance of other nitrogenous fertilizers may be compared. It should, however, be mentioned that under certain circumstances sulphate may cause injury to crops, particularly if applied in dry weather. For this reason it is used successfully in dry weather to kill flat-leaved weeds on lawns.

Ammonium Chloride

Although ammonium chloride has not been used on the commercial scale as a fertilizer, its properties have been studied.⁵¹ Weight for weight, it contains a greater quantity of nitrogen than does sulphate (26.2 per cent. as against 21.2 per cent.) but, in its general properties, it resembles sulphate. Its ammonia is absorbed into the soil particles and subsequently nitrified and the hydrochloric acid liberated acts upon the calcium carbonate in the soil to form calcium chloride which is washed away in solution. On a nitrogen basis the effect of ammonium chloride on the yield of crops is very much the same as that of sulphate but there are a few significant variations. For instance, it appears to be slightly better than sulphate for grain crops and, possibly, for sugar beet, but, on the other hand, it is inferior for potatoes.

In general, then, ammonium chloride may be regarded as equal to ammonium sulphate as a fertilizer and, if it were found possible to manufacture it more cheaply (on a nitrogen basis) than sulphate, there would appear to be no reason why the fertilizer market should not be open to receive it.

Ammonium Bicarbonate

This substance contains a smaller percentage of nitrogen than does ammonium sulphate (17.8 as against 21.2); hence about 1.2 tons of bicarbonate must be used to obtain the same amount of nitrogen as in one ton of sulphate. This would involve slightly increased carriage charges and costs of application to the soil.

It has been said that differences in the behaviour of ammonium salts as fertilizers will in the main be associated with differences in the anion or acid radical of the salt. Some probable differences between bicarbonate and sulphate become at once apparent on considering the properties of the bicarbonate ion, on the one hand, and the sulphate ion on the other. The bicarbonate ion, for instance, will not react with calcium carbonate in the soil, hence the use of am-

monium bicarbonate will not have the same acidifying effect on soil as has the use of sulphate. Although this is not likely to be important in a single season, or in many seasons in chalky soils, the effect is cumulative and it can be calculated that, by replacing 1 ton of sulphate by 1.2 tons of bicarbonate, 0.42 tons less of lime (CaO) will be required at some future date.

Again, in contrast to sulphuric acid, carbonic acid is a very weak acid and its salts are dissociated to some extent in solution. A solution of ammonium bicarbonate, therefore, contains free ammonia and this opens up two possibilities; (a) the free ammonia may be lost by volatilization from the soil before it is adsorbed into the soil particles and (b) a solution containing free ammonia may have a toxic effect upon seeds, plants and soil organisms. These possibilities have been borne in mind during investigations which have been made on the use of ammonium bicarbonate as a fertilizer, particularly since it can be assumed, on general grounds, that if such effects were non-existent or could be avoided then bicarbonate should be as effective a fertilizer as sulphate.

Several workers have tested ammonium bicarbonate, though they applied it to the soil in the way which is normal for sulphate,⁵² and have demonstrated that it is a useful fertilizer; they could not say whether or not it is as good as sulphate. Other investigations have been made on specific points⁵³ and, from these, the conditions of application necessary for the most efficient use of ammonium bicarbonate as a fertilizer have been determined. It appears that if bicarbonate is applied to the soil in the usual way, that is, on the surface, a considerable proportion of the ammonia is lost to the atmosphere. The rate and total amount of loss depends to some extent on the weather conditions, the uniformity of application and the character of the soil but, on average, about 50 per cent. of the ammonia is rendered ineffective as a fertilizer because it is lost by volatilization. It would therefore be expected that fertilizer trials, in which the bicarbonate was applied on the surface of the soil, would indicate that this compound was only about 50 per cent. as effective as sulphate, but most of the trials which have been carried out gave values considerably in excess of this figure. No satisfactory explanation of this has been suggested. The only simple way of preventing loss of ammonia appears to be to apply the bicarbonate beneath the surface of the soil. This is not difficult, since it could be "sown" in drills, as are seeds, and covered with soil immediately. Such a procedure would, however, add to the cost of application.

When bicarbonate was applied to soil in which plants were already growing, some damage to the leaves sometimes resulted. This, in addition to the ammonia loss which must occur under such conditions, shows that bicarbonate is not a suitable fertilizer to use after growth has started.

When bicarbonate was applied in contact with seed beneath the level of the soil, some retardation and, in some cases, actual prevention, of germination occurred. This effect depended on the kind of seed and on weather and soil conditions. A similar effect was also obtained with ammonium sulphate and the bicarbonate effect was sometimes greater than and sometimes less than that shown by sulphate. When the salt was applied below the level of the soil but out of contact with the seed, germination was unaffected yet the fertilizer was shown to be immediately available for the plant when growth began. Such a method of application should be very satisfactory, since loss of ammonia is avoided, detrimental effect on the seed is prevented and the fertilizer is available when required. Having regard to the results of experiments made under conditions not nearly so favourable as those just described, there is strong reason to believe that, when so applied, ammonium bicarbonate would give results at least equal to those given by sulphate of ammonia. Machines for applying the fertilizer beneath the soil at each side of the seed drill have been designed in America but are apparently not in use in this country.

The fertilizing properties of ammonium bicarbonate have been dealt with at some length because, in its manufacture, the use of an expensive acid is avoided. It seems probable, therefore, that bicarbonate could be produced more cheaply than sulphate. Its large scale use as a fertilizer, however, appears to depend upon the development of a new technique in the application of fertilizers to the soil. When suitable machines are in use, it may be that ammonium bicarbonate will prove a most satisfactory nitrogenous fertilizer.

Concentrated Gas Liquor

Concentrated gas liquor is probably the most cheaply prepared ammoniacal commodity, containing, as it does, 15 per cent. or more of its weight of ammonia. At first sight, it seems a most unpromising product for use as a fertilizer but its cheapness warrants its consideration.

Its obvious disadvantages are that it is difficult to handle except in specially designed apparatus and that its pungent odour would undoubtedly cause an initial prejudice against it. Also, since it could probably only be applied to the land at one part of the year, the provision of adequate storage capacity might be expensive. It is of variable composition and, on the average, its ammonia content is not more than two-thirds that of sulphate of ammonia.

The most obvious advantage of concentrated liquor, as has been pointed out, is its cheapness, but it has other points in its favour. One is that it can be prepared almost as cheaply on small as on large Works, so that centralized production is not necessary to secure its economical manufacture. This would reduce transport costs in the case of Gas Works situ-

ated near agricultural areas. Also, it shares with ammonium bicarbonate the advantage over sulphate that it does not remove lime from the soil. So far as is known, no large-scale trials have been made on the use of concentrated gas liquor as a fertilizer but investigations on a small scale⁵⁴ have given valuable indications as to the conditions for its effective use.

It is well known that concentrated liquor contains volatile ammonia which it loses relatively rapidly on exposure to air. It would, therefore, be expected that considerable ammonia loss would occur when the liquor was applied to the surface of the soil. Investigation has shown that the extent of this loss is no greater than that from ammonium bicarbonate and is smaller if the liquor is diluted before application. As with ammonium bicarbonate, application of concentrated liquor beneath the surface of the soil prevents appreciable loss.

Investigation has also been made on the toxic effect which concentrated liquor may have on seeds and growing plants. As a top dressing for growing plants, concentrated liquor was generally useless, the plants being severely scorched and sometimes killed. When the liquor was applied to the surface of grassland, however, recovery from scorching was rapid and the fertilizing effect of the liquor was soon manifest, new grass growing rapidly, uniformly and relatively free from weeds. A toxic effect on seeds was also noticed when these were sown in contact with the liquor but, in the majority of experiments, the effect was noticeably less than that of sulphate in similar circumstances. As with ammonium bicarbonate, application below the soil surface but out of contact with the seed prevented toxic effect and provided nitrogen for the plant in a readily available form. If the material were applied in such a way there is strong reason to believe that equality of performance with sulphate would be obtained. Before such practice could be adopted on the large scale, however, it would be necessary to put on the market machines which would, in the same operation, sow and cover the seed and apply and cover the concentrated liquor at each side of the seed drill.

Crude Ammoniacal Liquor

This is the cheapest ammoniacal substance of all, since its production is a necessary part of the normal coal gas making process and its cost may therefore be debited to that process. It is, however, a relatively weak solution of ammonia, containing only 1.5 to 2 per cent. of total nitrogen or, approximately, one-tenth to one-fifteenth the amount present in sulphate of ammonia. Nevertheless, on a nitrogen basis, its value delivered to the farmer's nearest station should be 9s. to 14s. per ton when sulphate is sold at £7 per ton. Its actual worth to the farmer depends, however, on the relative costs of distribution and above all on its efficiency as a fertilizer compared with that of sulphate.

This subject has been studied by several people and a number of trials on a practical scale have been made.⁵⁵ Crude ammoniacal liquor differs from concentrated gas liquor in two important respects, apart from its smaller ammonia content:

- (i) It contains a proportion of fixed ammonia, which could not be lost from the soil by volatilization.
- (ii) It contains, relative to the amount of ammonia, a much greater proportion of other bodies, phenols, thiocyanate, etc., which might have an adverse effect on plants.

The presence of fixed ammonia is an advantage to crude liquor and experimental determinations have indicated that the amount of ammonia lost by volatilization is considerably smaller than that lost from either concentrated liquor or ammonium bicarbonate.⁵⁶ Generally 20 to 25 per cent. is lost, a proportion which in many cases would not be serious. Covering the liquor with a shallow layer of soil again prevents loss.

As a top dressing, ammoniacal liquor is not suitable except with grassland. With meadow hay⁵⁷ its application gave a greatly increased yield and a reduction in the number of weeds. With other growing crops, surface application resulted in severe damage and some mortality. There is also a toxic effect when ammoniacal liquor is applied in contact with seed and this toxic effect is much greater than that caused by concentrated liquor, ammonium bicarbonate or ammonium sulphate. It is due, in the main, to ammonium thiocyanate which is well known as a plant poison. This compound is, however, oxidized (probably to ammonium sulphate) by the soil organisms during the course of one or two weeks and the toxic effect can therefore be avoided by applying the liquor to the soil at least a fortnight before sowing. It can also be reduced by cultivating the ground between applying liquor and sowing seed and almost entirely eliminated by applying the liquor beneath the soil but out of contact with the seed.

It is possible that, in certain circumstances, ammoniacal liquor may be useful for ridding soil of certain pests. The benefit accruing on ground infested with eel-worm was demonstrated in a striking way in an experiment described by A. L. Holton.⁵⁸

The possibility of disposing of ammoniacal liquor by spreading it over the surface of land has previously been discussed. It is now apparent that the fertilizing effect of the liquor is considerable, provided that the necessary precautions in its application are taken. These are (a) that contact of the liquor with living plants, except grass, should be prevented, and (b) that contact of the liquor with seeds should be avoided until absorption of ammonia into the soil is complete and oxidation of thiocyanate has occurred. It will therefore be seen that the most suitable time of the year for the applica-

tion is between October and March. Having regard, however, to the fact that there is a tendency for nitrogen to be washed out of the soil during the autumn months, it would be preferable, from the point of view of efficient fertilization, to apply in late winter or early spring.

Ammonium Phosphate

Several proposals have been made for the fixation of Gas Works ammonia as ammonium phosphates. These compounds are fertilizers in a double sense, both the nitrogen and phosphorus being plant foods. They come, therefore, under the heading of a new class of fertilizers, the so-called "concentrated fertilizers". These have only been developed recently and have not been fully investigated. They would be expected to have an effect equal to that of mixtures of simple fertilizers containing the same quantity of plant food and such tests as have been carried out indicate that, in general, this is so.

X RECOVERY OF AMMONIA AS AMMONIUM SULPHATE WITH THE USE OF SULPHURIC ACID INDIRECT PROCESS

Brief mention has already been made (Section III) of the indirect process for the production of ammonium sulphate from ammoniacal liquor. The process has been in operation at Gas Works for a long period of years and the basic principles of plant design and operation have long been more or less standardized, though it remains generally true, in this as in many other cases, that the more modern the plant the greater its efficiency. The great majority of Gas Works technicians are therefore well acquainted with the construction and working of sulphate of ammonia plants, which do not require any more detailed description here than that already given. What will be considered are the economics of the process and possible methods whereby the cost of the production may be reduced.

Cost of Ammonium Sulphate Manufacture

In the Second Report of the Ammonia Sub-Committee the cost of production of ammonium sulphate from ammoniacal liquor was calculated from data provided in 1929 by a number of Gas Undertakings. The items of cost there given are repeated in Table 16. It is realized that these may not be strictly correct at the present time but this is not of great importance since (a) variations in cost between different Works are greater than any variation due to a change in the general price level and (b) the primary reason for the inclusion of the table is to provide a basis by which the effect of economies in various directions can be assessed.

Bases of Costs

1. *Steam*.—It is assumed that the total ammonia is recovered from the liquor which is taken as being of 10 oz. strength, and that the amount of steam used is one-third of the weight of the liquor. The efficiency of conversion of ammonia to sulphate is taken as 95 per cent.
2. *Lime*.—The lime requirement is calculated on the assumption that the amount of fixed ammonia is 20 per cent. of the total, that the lime used contains 96 per cent. of CaO and that the quantity of lime used is 20 per cent. greater than that theoretically required.
3. *Sulphuric Acid*.—The weight of acid (75 per cent. H_2SO_4) required per ton of sulphate is 0.99 ton.
4. *Capital Charges*.—These, per ton of sulphate made, will obviously vary considerably with the capacity of the plant and the proportion of the year during which it is in operation. The average for a number of Works is taken.

5. *Labour, Supervision, etc.*—These costs are also subject to considerable variation and the figure taken represents what is considered to be a reasonable average.

It should be repeated that it is not justifiable to take these figures as representing the general average costs. The cost of raw material has fluctuated and the manufacture of sulphate has been centralized to a considerable extent since 1929, and the effect of this on the average cost of production cannot be assessed without full enquiry. The importance of the table is that, in it, the cost of sulphate manufacture has been itemized and it becomes easier, in consequence, to assess the effect on the cost of production of various modifications of practice which may be suggested.

Steam

According to Table 16 the cost of steam is only 14·5 per cent. of the total cost of sulphate manufacture. It would,

TABLE 16.⁵⁰—*Cost of Manufacture of One Ton of Sulphate of Ammonia from 10 Oz. Liquor (20 per Cent. Fixed Ammonia)*

	£	s.	d.
Steam.—4·16 tons at 4s. per ton	0	16	8
Lime.—238 lb. (96 per cent. CaO), at £1·75 per ton ..	0	3	9
Acid.—1 ton (75 per cent. H ₂ SO ₄) at £3 per ton ..	3	0	0
Maintenance, depreciation, etc. of plant	0	14	0
Labour, supervision, etc.	1	0	0
Total	£5	14	5

therefore, at first sight appear that economies possible in this direction are only small in magnitude. This is actually not so, as will be shown, and such economies are well worthy of consideration.

Apart from its use for subsidiary purposes, such as pumping, preparing milk of lime, etc., steam is required in the process for the distillation of the ammoniacal liquor and it may be assumed, although not with strict accuracy, that the amount of steam required is proportional to the amount of liquor to be distilled. Expressed as per ton of sulphate the steam required is obviously inversely proportional to the total concentration of ammonia in the ammoniacal liquor.

Table 17 gives, for liquors of varying total ammonia content, the volume of liquor required to produce one ton of sulphate (95 per cent. conversion efficiency) and the cost of steam for distillation, again assuming that the amount required is equal to one-third of the weight of liquor to be distilled.

The range of concentration of liquors taken in Table 17 has purposely been made rather wider than is normally experienced. It may be taken that most Gas Works produce liquor of between 6 and 16 oz. strength and, within this range, it will be seen that the cost of distillation varies by more than

17s. per ton of sulphate. The economies made by producing liquors of as great an ammonia content as possible are therefore apparent.

In addition to reducing the steam requirements per ton of sulphate of ammonia, increasing the strength of the liquor has other financial advantages. Since the total ammonia yield per ton of coal cannot well be varied, an increase in the ammonia content of the liquor must be accompanied by, and indeed caused by, a reduction in the quantity of liquor made. Such a reduction also results in economy in pumping, in transport (if transport other than by pumping is required), in storage accommodation and in water.

No precise figures appear to be available for the average cost of pumping liquor from storage to the sulphate plant or to tanks in which it is taken to the sulphate plant, but it will generally not be great. The cost of transport to a dis-

TABLE 17.—*Steam Requirements of Different Strength Liquors*

Strength of Liquor.		Gal. of Liquor per Ton of Sulphate.	Cost of Steam in Shillings per Ton of Sulphate.
Oz.	G. Total NH ₃ per 100 C.c.		
1	2	3	4
4	0.87	7,000	41.5
6	1.30	4,670	27.6
8	1.74	3,500	20.8
10	2.17	2,800	16.6
12	2.60	2,330	13.8
14	3.04	2,000	11.8
16	3.47	1,750	10.4
18	3.90	1,550	9.2
20	4.34	1,400	8.3

tant chemical works, where this is necessary, may, however, amount to more than £1 per 1,000 gal. of liquor or, for a 10 oz. liquor, to £3 per ton of sulphate. At such a figure, the production of sulphate must, at the present time, result in financial loss and therefore this method of dealing with the liquor is now only resorted to in exceptional circumstances. In these cases there is urgent need for reducing the volume of liquor as much as possible. The cost of storage of liquor has been estimated to average 2s. per 1,000 gal. and the cost of water about 1s. per 1,000 gal.⁶⁰

Accepting these figures for storage and water, neglecting pumping and transport charges but including cost of distillation, it can be calculated that the saving effected by reducing the volume of liquor by 1,000 gal. is about 9s. Furthermore, the smaller the quantity of ammoniacal liquor produced, the smaller is the volume of the resulting effluent liquor and, in general, the easier it is to dispose of this waste product.

Methods of reducing the volume of liquors, both ammonia-

cal and spent, have already been dealt with (p. 64). So far as these also increase the strength of the ammoniacal liquor they also reduce the steam consumption in sulphate manufacture. The most direct way of obtaining decreased volume and increased strength is to reduce or eliminate the volume of clean water used in the scrubbers. The maximum strength of liquor obtainable by this means is represented by the yield of ammonia divided by the weight of virgin liquor produced. For Durham coals carbonized without steaming this strength is about 18 oz.,⁶¹ 1,550 gal. of such liquor being required per ton of sulphate. For Durham and Yorkshire coals carbonized in vertical retorts and steamed to yield gas having a calorific value of 510 B.Th.U. per cu.ft., this strength is reduced to about 11 oz. by the steam which passes through the retorts undecomposed, and the amount of liquor required per ton of sulphate is increased to 2,540 gal. In order to produce such liquors and, at the same time, efficiently strip the gas of its ammonia, it is necessary that the condensing and scrubbing plant should be highly efficient and it may also be necessary to treat the virgin liquor so as to increase its content of carbon dioxide.

The cost of increasing the condensing plant by 25 per cent. has been estimated to be of the order of 3s. 3d. per ton of sulphate made.⁶² Such an increase would, in many cases, result in an increase in the actual capacity of the existing washers, but these themselves could be increased in size by 25 per cent. by the expenditure of an amount corresponding to 2s. 6d. per ton of sulphate. The cost of such increases would, in many cases, be substantially lower than the savings effected.

It should be borne in mind that no washing process which uses weak ammoniacal liquor as the washing liquid can completely remove the ammonia from the gas; a small fraction must remain in the gas entering the purifiers. It is, however, customary to allow a small proportion to go forward, so that the monetary value of the whole of that quantity allowed to pass forward when weak liquor is used as the scrubbing reagent should not be debited to the cost of adopting this medium. In any case, the money value of 5 gr. ammonia per 100 cu.ft. of gas, which is the amount usually allowed to pass when weak liquor is used, is only about 2s. per ton of sulphate of ammonia made.

Lime

The cost of lime in the case quoted in Table 16 was only 3 per cent. of the total cost of sulphate manufacture. Any possible economies in the liberation of the fixed ammonia must, therefore, inevitably be slight and need not be considered. It is, however, necessary to discuss here the economics of the recovery of fixed ammonia. The discussion will have reference to ammonia recovery only, it having previously been shown that removal of fixed ammonia should generally

facilitate disposal of the spent liquor.

By making certain assumptions in addition to those already stated, it is possible, from the data given in Table 16, to calculate separately the costs of sulphate manufacture from the free and from the fixed ammonia. In this calculation, which is set out in Table 18, the different items of cost have been allocated partly to the free and partly to the fixed ammonia. The cost of acid has been proportioned according to the relative quantities of free and fixed ammonia; that of lime has been debited entirely to the fixed ammonia; the labour, maintenance and depreciation costs for fixed ammonia recovery have been taken as 10 per cent. greater per ton of sulphate than the corresponding costs for free ammonia, owing to the added complication of the liming arrangement for liberating the former.

TABLE 18.—*Cost of Manufacture of Sulphate of Ammonia from Free and Fixed Ammonia (10 Oz. Liquor, 20 per Cent. Fixed Ammonia)*

—	Total Cost per Ton of Sulphate.	Cost of 0·8 Ton Sulphate from Free Ammonia.	Cost of 0·2 Ton Sulphate from Fixed Ammonia.
1	2	3	4
	£ s. d.	£ s. d.	£ s. d.
Steam.—4s. per ton	0 16 8	0 11 7	0 5 1
Lime.—£1·75 per ton	0 3 9	—	0 3 9
Acid.—£3 per ton	3 0 0	2 8 0	0 12 0
Maintenance, depreciation, labour, etc.	1 14 0	1 6 7	0 7 5
Total	5 14 5	4 6 2	1 8 3
Cost per ton of sulphate from free ammonia	5 7 10
.. fixed	7 1 3

It will be seen that the cost of recovery of fixed ammonia as sulphate works out at over £7 per ton, 33s. more than that for the free ammonia. This, however, does not mean that it is no longer economical to recover the fixed ammonia when the price obtained for sulphate falls below £7. At most Undertakings which have, during the past few years, experienced losses in ammonia recovery, a sulphate plant was already in existence and depreciation and other fixed charges had to be borne whether much or little sulphate was produced. On the other hand, labour and maintenance costs are undoubtedly reduced by discontinuing the use of lime, but not in proportion to the reduction in yield of sulphate. In the following calculation it is assumed that the total depreciation, labour, etc., charges are reduced by 10 per cent. by discontinuing the recovery of fixed ammonia. A 10 oz. liquor is again taken as an example, but a fixed ammonia content of 40 per cent. is assumed. The costs of ammonia recovery with and without liming are given in Table 19.

It is apparent that in this particular case, which is probably typical, it is more expensive per ton of sulphate to recover the free ammonia only than to recover the total. If, therefore, sulphate manufacture shows a profit it is obviously desirable to recover fixed ammonia where suitable plant is already in existence. If the plant is operated at a loss, it will be economical to cease liming only when the loss on total ammonia recovery per ton of sulphate multiplied by the number of tons produced exceeds the greater loss on free ammonia recovery per ton of sulphate multiplied by the smaller number of tons produced. In the case instanced, it would not be profitable to discontinue the recovery of fixed ammonia until the price obtained for sulphate fell below £5 8s. 1d. per ton.

The purpose of the foregoing argument is not primarily to bring forward precise figures, which depend on a great variety of circumstances, but rather to show that it may still be de-

TABLE 19.—*Cost of Manufacture of Sulphate of Ammonia from Free and Total Ammonia (10 Oz. Liquor, 40 per Cent. Fixed Ammonia)*

—	Total Ammonia per Ton of Sulphate.	Free Ammonia per 0·6 Ton of Sulphate.
1	2	3
	£ s. d.	£ s. d.
Steam	0 19 11 (40 per cent. of liquor)	0 11 7 (23 per cent. of liquor)
Lime	0 7 6	—
Acid	3 0 0	1 16 0
Maintenance, depreciation, labour, etc.	1 14 0	1 10 6
Total	6 1 5	3 18 1
Total, per ton of sulphate	6 1 5	6 10 0

sirable to recover as much ammonia as possible even when a loss is sustained in so doing.

It will be appreciated that the situation would be entirely different if the installation of a new sulphate of ammonia plant were being contemplated. It would require much more favourable circumstances to justify the installation of a plant designed for the recovery of the total ammonia than to justify the continued operation of a plant already in existence. Probably for this reason the great majority of the ammonia plants erected in recent years are intended to deal with free ammonia only.

It has also been suggested that ammonia recovery may be cheapened by suitable selection of liquors, so that only those containing relatively large concentrations of ammonia are distilled, other much weaker liquors being otherwise disposed of. The process described on p. 68 achieves this end. In certain circumstances the adoption of such a system may be profitable, but an analysis of the situation in a manner similar

to that already given would be necessary before a final verdict could be reached.

Sulphuric Acid

The cost of sulphuric acid constitutes by far the largest item in the conversion of gas works ammonia into sulphate. In the example quoted in Table 16 the cost of acid amounts to 52 per cent. of the total cost. It is here, therefore, that one may justifiably look for considerable economies, but it is immediately apparent that such economies must not be expected if the acid is purchased at the market price. At the same time, it must be remembered that the price of sulphuric acid is bound up with that of spent oxide and that it is quite likely that a Gas Works which purchases sulphuric acid for ammonia recovery may receive a higher price for spent oxide than one which does not. Such a Works may feel entitled to credit this difference in price to the sulphate of ammonia plant.

It appears, however, that for any great economy to be effected in the cost of sulphuric acid it would be necessary for the acid to be manufactured at the Gas Works, using spent oxide as a source of sulphur. The devil gases from the sulphate plant might also be used to provide the sulphate radical, but the quantity available would not produce sufficient acid for the whole of the ammonia. Some Gas Works already operate acid plants but if, in such cases, the product can be disposed of in the open market it could not economically be diverted to the sulphate plant at a price lower than that already obtained.

It has been suggested⁶³ that Gas Works which now purchase acid should install acid plants which would be combined with the sulphate plant in such a way as to reduce labour to a minimum. Such a combined installation could be regarded as one economic unit and might be profitable to work in circumstances where the purchase of acid would entail a loss on the process. This suggestion appears worthy of examination.

Labour, Maintenance, etc.

Labour costs in the manufacture of ammonium sulphate represent a large item. No doubt this could be reduced by the adoption of plants of a more automatic type but the most effective way of reducing labour costs is to work on a bigger scale. When the capacity of a plant is increased, the increase in labour and supervision charges is not in proportion and, generally speaking, the larger the plant the cheaper is the labour cost per ton of product. Similarly, the capital cost of a plant does not increase in proportion to its capacity and therefore the interest and depreciation item in the costs per ton of product is smaller the larger the plant. Considerable

economies in the manufacture of sulphate could therefore be expected if this were carried out on a larger scale. Unfortunately this cannot be done on each Gas Works, since the amount of ammonia produced in the carbonization of its coal is limited. It can, however, be carried out at centrally situated works, whether Gas Works or chemical works, if these can be provided with the ammonia from neighbouring Gas Works. Transport of ammoniacal liquor is, however, expensive on an ammonia basis and only in few cases would the economies of centralized manufacture be sufficient to justify the transport of ammoniacal liquor over more than short distances. The only way of cheapening the cost of transport is to obtain the ammonia in a form more concentrated than that in which it occurs in crude liquor and this can be done by manufacturing "concentrated gas liquor". This product, which usually contains 15 to 22 per cent. of ammonia, can now be prepared in entirely automatic plants and, as long ago as 1930, the Ammonia Sub-Committee of The Institution of Gas Engineers was of the opinion that "it would appear that with centralized sulphate plants the local production of concentrated liquor might pay".⁶⁴ Since that time a large number of concentrated liquor plants have been erected and the subject has become of sufficient importance to require a special Section (p. 113).

It may be concluded that, in order to reduce capital and labour costs per ton of sulphate to a minimum, it is necessary to work on as large a scale as possible. For all but large Gas Works, this involves the production of sulphate at a centrally situated point. This will almost invariably be a Works which has its own sulphuric acid plant and it may well find it economical to sell acid to the sulphate plant at a low figure. The cost of production per ton of sulphate at such a Works must be much less than when prepared on a smaller scale with an external source of the necessary acid.

SEMI-DIRECT PROCESS

Very few Gas Undertakings in this country operate the semi-direct process of ammonia recovery, though the process is in operation at a number of coke oven installations. The gas leaving the retorts or ovens is first subjected to preliminary condensation and efficient tar extraction and is then passed through exhausters direct to a saturator where it comes into contact with sulphuric acid. From the saturator, the gas, now ammonia-free, passes through final condensers and thence to the purifiers. The virgin liquor from the retort house and primary condensers is distilled in the ordinary way, the resulting ammonia gas being introduced into the stream of coal gas passing to the saturator.

When this process was put into operation at a Gas

Works⁶⁵ serious difficulties were encountered but these were subsequently overcome and the process then worked satisfactorily. Compared with the indirect process, the semi-direct process requires less liquor storage capacity (since the process is continuous), produces a smaller volume of spent liquor containing only small quantities of thiosulphate and thiocyanate, eliminates the necessity for ammonia scrubbers, and requires rather less steam for distillation. On the other hand, the semi-direct process requires the provision of secondary condensers, requires more power for the exhausters (since the whole of the gas has to pass through the saturators), necessitates the use of more than one saturator (in order to deal with different rates of gas production), and allows a greater quantity of hydrogen sulphide to pass to the purifiers.

The capital cost of a new installation is much less for the semi-direct process than for the indirect. This is due entirely to the saving in respect of scrubbers and storage tanks since, apart from these, the semi-direct process is the more expensive. It would appear that there is little difference in the running costs of the two types of plant. On the whole, it may be said that the semi-direct process might appeal in the case of an entirely new Gas Works but, where adequate storage and scrubbing capacity is already available, the indirect would be preferred.

DIRECT PROCESS

In this country, the direct process is operated only in coke oven plants. After leaving the carbonizing chambers, the crude gas is first effectively freed from all tar fog at a temperature of about 75° C. To aid this removal and also to remove ammonium chloride, hot liquor is usually sprayed into the tar extractors. This liquor is recirculated until it attains a high concentration of ammonium chloride and is then evaporated for the recovery of this compound. After passing the exhausters, the gas, still maintained above its dew-point, is forced through saturators for the extraction of ammonia by sulphuric acid with the formation of ammonium sulphate, which is separated in the usual way. The gas leaving the saturators is then cooled and, if required for distribution, purified in the normal manner, no washers or scrubbers being, however, required.

The advantages of direct ammonia recovery are that no ammoniacal liquor is produced, no liquor storage capacity needs to be provided and no ammonia still is required. More power is required by the exhausters, since they have to work on a gas at a high temperature and against the back pressure thrown by the saturator, and the product is liable to contamination with tar. No information is available as to the behaviour of a direct ammonia recovery plant on a Gas Works, where the rate of gas making fluctuates, but it does

not appear that it would present a net advantage over the indirect process.

It should be mentioned that the liquor condensing in the condensers after the saturator would have a composition similar to that of an ordinary spent liquor, except that its volume might be smaller and its thiocyanate and thiosulphate contents very low.

XI THE UTILIZATION OF AMMONIA FOR THE PURIFICATION OF COAL GAS

The process now almost universally used for the removal of hydrogen sulphide and hydrogen cyanide from crude coal gas, namely, the iron oxide process, necessitates plant occupying a great deal of ground space and entails a large capital expenditure. An alternative and less cumbersome method has long been sought and many ingenious systems have been and are still being devised. Some of these have been tried out on the large scale, but none has as yet shown the reliability of the iron oxide process. It is not the purpose of this Section to deal with these suggested processes except as regards their possible contribution to the solution of the ammonia problem. This they might do in either or both of two ways:

- (1) They might use ammonia in their operation and thus provide an outlet for this product other than the open market;
- (2) Their operation might lead to the production of some ammonium salt, preferably sulphate, and thus effect ammonia recovery without the use of sulphuric acid. In assessing the economics of any process of this second class, it is necessary to regard ammonia recovery and gas purification as one economic system and to compare the net cost of the new process with the sum of the net costs of ammonia recovery and gas purification as at present carried out.

Several such processes have been examined by the Ammonia Sub-Committee of The Institution of Gas Engineers and the following brief accounts are in the main abstracted from the Reports of that Committee:

THE ZINC PROCESS

This process,⁶⁶ due to Prof. J. W. Cobb, may be divided into three stages. The first consists in passing the crude gas, while still above the dew-point, through a hot solution of zinc sulphate. The ammonia and an equivalent quantity of hydrogen sulphide react with the zinc sulphate, producing zinc sulphide in suspension and ammonium sulphate in solution. The former is recovered by filtration and the latter by evaporation. The second stage consists in the roasting of the zinc sulphide in air to produce zinc oxide and sulphur dioxide, and the third in the passing of the gases from the roasting process, together with excess air, through an aqueous suspension of the zinc oxide from a previous roasting. Here zinc sulphate is regenerated and its solution is then re-used for the extraction of the crude gas.

On the practical scale it was found that this third stage of the process proceeded only very slowly and no means were found of increasing its velocity. The costs of blowing air for

oxidation purposes were therefore heavy and the economic success of the process doubtful on that account. In addition, the fact that a sequence of operations was necessary implied that labour costs would be relatively high, particularly for a small plant.

THE BURKHEISER PROCESS

This process⁶⁷ aims at the complete removal of hydrogen sulphide, hydrogen cyanide and ammonia from crude coal gas and the production from these of a salt of ammonia suitable for fertilizing purposes. The underlying principles of the process as originally proposed were as follows:

The gas from the carbonizing system was cooled and freed from tar in the usual way, the condenser liquor being worked up and the ammonia returned to the gas stream as in the semi-direct process. The crude gas, which contained all its original ammonia, sulphide and cyanide, was first freed from the two last-mentioned substances in a "dry" purifier containing a special form of hydrated oxide of iron. The hydrogen sulphide was converted into ferric sulphide and the hydrogen cyanide into ammonium thiocyanate, and the activity of the oxide was so great that the gas speed could be 25 to 30 times the normal rate. The fouled oxide was revived in the purifier itself by the agency of a regulated current of air. Oxidation took place in the usual way but the temperature rose sufficiently to cause the liberated sulphur to burn, producing sulphur dioxide. At the same time the thiocyanate was converted into ammonia, which resulted in an increase of 8 to 10 per cent. in the amount of ammonia recovered per ton of coal. The heat generated during revivification was controlled by circulating water, the heated water being used to warm the working purifiers.

The gas leaving the purifiers was led up a tower, the "gas" scrubber, where it was stripped of its ammonia by a countercurrent stream of a solution of ammonium bisulphite and bisulphate. This solution absorbed the ammonia with avidity and a neutral solution of ammonium sulphite and sulphate was formed. This was then passed to another similar tower, the "air" scrubber, where it was brought into contact with an upward flowing stream of gases from a purifier undergoing revivification. Here it was converted by the sulphur dioxide and excess air into a mixture of ammonium bisulphite and bisulphate, which was then re-used in the "gas" scrubber. When the solution became saturated crystallization took place and a mixture of ammonium sulphite and sulphate containing 50 to 65 per cent. of the latter separated. This could itself be used as a fertilizer but, if desired, it could be converted entirely into sulphate by an air oxidation process.

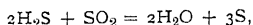
Several experimental plants for the operation of the Burk-

heiser process were erected but all encountered the revivification of the oxide. The reaction was so violent that the material became red-hot and broke into dust, so that it became useless for further purification. In order to overcome this difficulty a modification of the process was introduced in which the purification process was a "wet" one, the hydrogen sulphide and cyanide being extracted from the gas by means of a suspension of ferric oxide and sulphur in ammoniacal liquor. Ferric sulphide in suspension and ammonium polysulphide and thiocyanate in solution were produced. The ferric sulphide was removed by settlement and revivified with hot air; the solution was heated to 95° C., whereupon the polysulphide decomposed, liberating free sulphur. This was burnt in a separate kiln to provide oxides of sulphur which were recovered in the "air" scrubber. The modification proved successful so far as purification was concerned but gave rise to difficulties in the handling, drying and revivification of the oxide. Accordingly, a further change was made and both purification and revivification became wet processes. In this final form of the process the method of purification remained as described above. The sludge produced, containing ammonium polysulphide and thiocyanate in solution and ferric sulphide and excess sulphur in suspension, was treated with concentrated gas liquor which dissolved the free sulphur. After settling out the ferric sulphide the solution was heated to 95° C. for the decomposition of the polysulphide and the sulphur produced was separated and burnt. The ferric sulphide sludge was then revivified by the agency of an air stream.

The process would appear to have many advantages over the usual methods of purification and ammonia recovery, including smaller capital cost, smaller space requirements, ease of operation and an internal source of an acid radical for the ammonia. It does not appear, however, to have made further headway but it is suggested that it is worthy of further examination.

THE FELD PROCESSES

Several processes⁶⁸ were devised by the late Walther Feld for the purification of crude coal gas. Of these the first attempted to use the reaction



the sulphur dioxide being dissolved in a tar oil in which the sulphur was also soluble. It was not a success, the slowness of the reaction and the recovery of the sulphur being the main difficulties.

A further process also produced elementary sulphur, namely, by the reduction of zinc thiosulphate by the hydrogen sulphide in the crude gas, the thiosulphate being regenerated

by the action of air and sulphur dioxide. This, too, proved unsuccessful, mainly on account of side reactions which took place and interfered with the cycle of operations.

In a third process, crude gas was purified by means of a solution of ferrous thiosulphate, this being converted by ammonium sulphide ($2\text{NH}_3 + \text{H}_2\text{S}$) into ferrous sulphide, ammonium thiosulphate being also produced. The ferrous thiosulphate was regenerated by the action of sulphur dioxide, sulphur being precipitated. When the concentration of ammonium salts in the liquid became sufficiently high, the solution was heated in a current of air and sulphur dioxide, whereupon the ferrous sulphide was oxidized to ferrous sulphate and ammonium thiosulphate was converted into ammonium sulphate. The solution was then again treated with crude gas to precipitate the iron as sulphide and, after filtration, the liquid was evaporated for the recovery of ammonium sulphate. Difficulties soon developed when the process was tried on a large scale. These were mainly caused by side reactions in the course of which the iron was converted into an inactive compound and the process, in consequence, failed to establish itself.

A fourth process devised by Feld avoided the use of metallic compounds altogether; it was based on the fact that both ammonia and hydrogen sulphide can be extracted from crude gas by solutions of polythionates, which can be regenerated by means of sulphur dioxide. The gas was washed with a solution containing trithionate and tetrathionate of ammonia, these being converted by the agency of ammonium sulphide into ammonium thiosulphate and, in the case of the tetrathionate, into sulphur in addition. Treatment with sulphur dioxide at 35° to 40° C. regenerates the polythionate and redissolves some of the sulphur. The process was continued until the concentration of polythionates was sufficiently high, whereupon they were decomposed, by boiling, into ammonium sulphate, sulphur and sulphur dioxide. The ammonium sulphate was then recovered.

Experimental work on this process was continued over a period of several years and it was found that the reactions were affected by the carbon dioxide present in the crude gas. In addition, the regeneration process proceeded only slowly, necessitating the use of large reaction vessels. The commercial success of the process was thus very doubtful.

LIQUID PURIFICATION OF COAL GAS BY MEANS OF AMMONIA

The removal⁶⁹ of the acidic impurities of coal gas, namely, hydrogen sulphide and carbon dioxide, by the use of the chief alkaline impurity, ammonia, is an attractive idea and one which has been well investigated. The process is not in itself, however, an outlet for the ammonia produced, since in theory this is all recovered as such. It does not result in the production of a saleable ammonium compound and the success of the process must

therefore depend on its efficiency as a purification system alone. The hydrogen sulphide and other acidic impurities are scrubbed from the gas by means of a concentrated ammonia solution prepared from ammoniacal liquor. The resulting solution of ammonium sulphide and other volatile salts is then fractionally distilled for the removal of hydrogen sulphide, etc., the ammonia being again recovered in the caustic form. Owing to the fact that the amount of acidic impurities greatly exceeds the amount of ammonia normally produced, it is necessary to circulate several times the amount of ammonia available in the gas. Ammonia losses are thus increased and this is one reason for the failure of the process. With the present low price of ammonia these losses might not be serious but other difficulties are encountered.

Compared with the oxide of iron method of purification, liquid purification by means of ammonia demands increased technical control, due to the necessity for the operation of a scrubbing plant, a distillation plant, which must be worked very carefully, and a Claus kiln, which effects recovery of sulphur. Also, it would not be economical to effect complete purification by the process and the use of oxide of iron catch boxes would, therefore, be necessary. It seems certain that the cost of operation of the process would be greater than that of the standard iron oxide method.

THE KOPPERS "C.A.S." PROCESS

This⁷⁰ is a development of one of the Feld processes. The crude gas is cooled and the virgin liquor worked up to a content of 10 to 12 per cent. of ammonia. Purification commences with the removal of hydrogen cyanide in a washer containing ammoniacal liquor and sulphur. In subsequent scrubbers, the ammonia and hydrogen sulphide are removed, the washing liquor being a solution of iron thiosulphate and polythionate with iron hydroxide in suspension. To this liquor is also added the 10 to 12 per cent. ammonia liquor prepared from the virgin liquor. The dissolved iron compounds absorb ammonia and hydrogen sulphide in the ratio of 2 to 1, forming iron sulphide and ammonium thiosulphate, the excess of hydrogen sulphide being removed from the gas by the suspended iron hydroxide. Part of the spent washing liquor is treated with sulphur dioxide for the regeneration of the soluble iron salts; part is treated with air for the conversion of the iron sulphide into iron oxide and sulphur. These two parts are then mixed and re-used in the washers. A third part of the spent washing liquor is settled, the supernatant solution of ammonium salts being treated with sulphur dioxide and then decomposed under pressure by the action of heat. A solution of ammonium sulphate is produced and the salt is recovered by evaporation.

It is obvious that the plant required for this process would be rather complicated and that careful technical control

would be required. It is also very doubtful whether the efficiency of hydrogen sulphide removal would be high enough to satisfy requirements in this country without the additional use of oxide of iron catch boxes. For this reason its commercial success in this country would be very unlikely.

THE "AUTO" PROCESS

A newer process⁷¹ of gas purification which uses ammonia but does not result in the production of an ammonium salt is the "Auto" process which has been operated on an experimental scale at the Billingham works of Imperial Chemical Industries. The scrubbing liquor contains, in solution, ferric ammonium ferrocyanide which is reduced by the hydrogen sulphide in the gas to the ferrous salt, sulphur being precipitated. The hydrogen cyanide in the gas is converted into ammonium thiocyanate and other salts and the ammonia is, to a large extent, taken up into solution. Regeneration of the ferric ammonium ferrocyanide is accomplished by blowing with air which, at the same time, volatilizes much of the ammonia from solution. The sulphur floats to the surface and is skimmed off and dried. The iron salts in the solution need occasional replenishment, for which purpose ferrous sulphate is used.

The purification is almost complete but catch boxes for the removal of the last traces of sulphide are necessary. The advantages of the process are claimed to be smaller capital costs, space requirements and back pressure. Moreover, there is no necessity to add air to the gas. It has not yet been established whether the total cost of the process would be smaller than that of the standard oxide system. The washing liquor has to be rejected periodically on account of its accumulated content of thiocyanate and thiosulphate and its disposal might prove difficult. In addition, the process suffers from the disadvantage of the wastage by discharge to atmosphere, of much of the ammonia, namely, that part which is usually recovered in the scrubbers and which it is the most economical to recover. The remainder of the ammonia, that in the condenser liquor, remains for disposal, so that the process cannot in itself be regarded as a solution of the ammonia problem.

GENERAL

If it be regarded as essential that gas works ammonia should be recovered in the form of ammonium sulphate, the sulphate radical may either be purchased from an external source or obtained from the sulphur in the crude gas. The latter course, if practicable, should provide the cheaper sulphate. The sulphur in the coal gas may be utilized by converting it into sulphuric acid, the acid being used for sulphate manufacture in the usual way, or some process may

be used which converts the ammonia and hydrogen sulphide in crude gas into ammonium sulphate without the necessity of preparing sulphuric acid.

This Section has been mainly concerned with processes of this nature. The conclusion is that it is by no means certain that such processes would be commercially successful, owing to their complexity, their sensitiveness to changes in conditions, their inability to remove the last traces of sulphide from the gas and other reasons. At the present stage of development, if it is desired to make an Undertaking self-supporting with respect to the acid radical in ammonium sulphate, it appears that the best method would be to manufacture sulphuric acid from the spent oxide from the purifiers. Although such a scheme might not appear to offer as great financial advantages as would other processes, it would have the practical advantages of being simple, easy to operate and not incompatible with the usual methods of gas washing and purification.

Methods of using gas works ammonia in the purification of coal gas without subsequent recovery of an ammonia product do not appear to offer sufficient advantages to justify the wastage of ammonia which they entail.

XII THE MANUFACTURE OF AMMONIUM BICARBONATE

It has already been shown that, in the recovery of gas works ammonia as ammonium sulphate, the greatest single item of expenditure is the cost of the sulphate radical when purchased as sulphuric acid. Examination was made in the preceding Section of possible methods of cheapening the cost of this radical but the conclusion was that no process had been shown to be more economical than, and as satisfactory as, that in which sulphuric acid is used. An alternative method of reducing this item of cost is to recover the ammonia not as sulphate but as some other salt of which the acid radical is considerably cheaper than the sulphate radical. One such salt which has been proposed is ammonium bicarbonate.

The chief advantage of ammonium bicarbonate is that the acid radical is already present as carbon dioxide in crude coal gas and, in this form, may be considered to be available without cost. The removal of carbon dioxide from crude gas would in itself be an advantage, since it has no heat value. A further advantage of ammonium bicarbonate is that the bicarbonate radical is not harmful to the soil, whereas the sulphate radical in ammonium sulphate tends to have an acidifying effect. The fertilizing properties of ammonium bicarbonate have been considered in Section IX and the conclusion was reached that, if the methods of application to the soil now used for ammonium sulphate were adhered to, the efficiency of bicarbonate would not equal that of sulphate but that, if special methods of application were developed, its value would be at least equal and possibly superior to that of sulphate. It may therefore be concluded that it would not at the moment benefit the Gas Industry to change over from sulphate production to bicarbonate manufacture, but that such a change over may be desirable at some future time. It may therefore be useful to record the various processes by which ammonium bicarbonate may be produced.

THE LEWIS PROCESS

In this process,⁷² as in the Parrish and MacLaurin processes (see paragraphs following), only part of the carbon dioxide necessary for the production of bicarbonate is obtained from the crude coal gas, the remainder being derived from some external source. Gas works ammoniacal liquor is distilled in the usual way, the distillation gases consisting of ammonia, carbon dioxide, hydrogen sulphide and excess steam, with smaller quantities of other gases. The amount of carbon dioxide will usually not be sufficient to convert the ammonia into ammonium bicarbonate, hence a further quantity of carbon dioxide is added in the form of waste gas from lime or Portland cement kilns or furnaces. It is assumed that the

mixture of this gas with distillation gases would, when cooled, deposit ammonium carbamate and that this could be converted into ammonium bicarbonate by the addition of water and a further amount of carbon dioxide. It is probable that conditions could be so controlled that ammonium bicarbonate would be deposited directly as such, as in the MacLaurin process, which is based on a similar principle.

THE MACLAURIN PROCESS

This process⁷³ consists in the distillation of gas liquor in the ordinary way, the extra carbon dioxide being supplied as flue gases introduced either hot, at the bottom of the still, or cold, at the top. The mixture of gases is cooled in a wide cooler and then bubbled through the condensate in a crystallizer where the bicarbonate is deposited. The latter is separated from the mother liquor and dried in a centrifuge. Unless the flue gases are freed from sulphur dioxide, the product will contain a small percentage of ammonium sulphite or sulphate.

It is not known if this process has been tried out on a practical scale, but there appears to be no reason why it should not work satisfactorily. The temperature of the gases leaving the still would need careful control so that an excess of steam is not carried forward. Any such excess would result in the accumulation of mother liquor which would require redistillation. It might, moreover, be difficult to separate the functions of the cooler and the crystallizer and it might be simpler to arrange for both processes to take place in one efficiently cooled vessel. A small scrubber would be needed for the removal of the traces of ammonia which would, no doubt, be contained in the gases leaving the crystallizer.

THE PARRISH PROCESS

One form of the Parrish process⁷⁴ differs from the MacLaurin process only in detail and by reason of the fact that the starting point is concentrated gas liquor and not crude ammoniacal liquor. The process is thus designed primarily for a central chemical works and not for the individual Gas Works. The concentrated gas liquor is distilled and the extra carbon dioxide added to the still gases in as concentrated a form as possible, suggested sources being saturator gases from a sulphate of ammonia plant, waste gases from a superphosphate plant, gases derived from the lime sludge of ammonia stills or flue gases. The mixture of gases is then cooled and ammonium bicarbonate crystallizes.

A second form of the process depends upon the fact that concentrated gas liquor contains sufficient ammonia to ensure that, when the latter is converted into bicarbonate, crystallization occurs and a large proportion of the ammonia is

deposited in this form. The conversion is effected by means of any of the carbon dioxide containing gases mentioned, in a tower down which the concentrated liquor flows. The crystallization is allowed to take place in tanks from which the crystals can easily be removed. The mother liquor is then distilled for the production of concentrated liquor which re-enters the process.

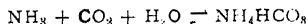
This process has been tried out on an experimental scale and appears to work without difficulty. A certain amount of care would be necessary in order to ensure that carbonation of the concentrated liquor is complete and that crystallization occurs in the right place. The gases leaving the carbonating tower would contain traces of ammonia which would, presumably, be recovered in a small scrubber. In common with the exit gases from the Lewis and the MacLaurin processes, these gases would also contain hydrogen sulphide and traces of hydrogen cyanide which it would be necessary to remove before the gases could be allowed to escape into the atmosphere.

PROCESSES WHICH USE THE CARBON DIOXIDE PRESENT IN CRUDE COAL GAS

In at least four processes for the manufacture of ammonium bicarbonate the whole of the necessary carbon dioxide is obtained from crude coal gas. These processes have an initial advantage over those previously considered, since removal of carbon dioxide from coal gas leads to a higher calorific value or, alternatively, enables more dilution with water gas to be effected in the attainment of the declared calorific value. This advantage is but small in relation to the tonnage of coal carbonized but is appreciable in relation to the tonnage of salt produced.

The important difference between carbonation by means of gases from an external source and carbonation by the agency of crude coal gas is that gases from an external source may be very rich in carbon dioxide, whereas crude coal gas contains only a small proportion, the concentration ranging between 1 and 6 per cent. depending on the system of carbonization used and the conditions of operation. The importance of this difference becomes evident after a study of the equilibrium conditions existing between ammonium bicarbonate in solution and in the gaseous phase in contact with the solution.

Ammonium bicarbonate is formed by the reversible reaction



and when equilibrium has been attained the following relationship between the concentrations [] of the reactants must hold:

$$\times [\text{CO}_2] \times [\text{H}_2\text{O}] = K$$

For a saturated solution at any given temperature $[\text{NH}_4\text{HCO}_3]$ is fixed by the composition of the solution and may for most purposes be included in the equilibrium constant K . Also, the concentration of the gases in solution is proportional to their concentrations, or partial pressures, in the vapour in equilibrium with the solution, so that the equation may be re-written

$$p\text{NH}_3 \times p\text{CO}_2 \times p\text{H}_2\text{O} = K_1$$

Over a fairly wide range of conditions at constant temperature the partial pressure of water vapour over a solution saturated with ammonium bicarbonate is also constant and may therefore be included in K , so that the equation becomes

$$p\text{NH}_3 \times p\text{CO}_2 = K_2$$

The value of the latter constant at different temperatures has been determined by W. K. Hutchison.⁷⁶ When the units are such that the concentration of carbon dioxide is expressed as a volume percentage and that of the ammonia in terms of gr. per 100 cu.ft. the value of the product K_2 is 984 at 20° C. and 158 at 10° C.

Now the gases in question will dissolve in a saturated solution of ammonium bicarbonate with consequential deposition of crystals of this salt only when the above values are exceeded in the gaseous phase. An average vertical retort gas contains, as it leaves the retort, approximately 200 gr. of (free) ammonia per 100 cu.ft. and 3 to 4 per cent. by volume of carbon dioxide. The product, which ranges between 600 and 800, is not great enough for solid ammonium bicarbonate to be formed at the temperature to which gas is usually cooled (about 20° C.), but would become so if the gas could be cooled to about 10° C. The whole problem of the utilization of the carbon dioxide contained in crude gas for ammonium bicarbonate manufacture is, therefore, to ensure that the product $p\text{NH}_3 \times p\text{CO}_2$ considerably exceeds the equilibrium value under the conditions of operation of the process. The problem has been solved in several ways.

The most obvious method is to lower the temperature of the crude gas to 10° C. or less. This would normally be too expensive unless it were necessary to cool the gas for some other purpose, *e.g.*, for naphthalene removal, benzole recovery or dehydration.

THE WILSON PROCESS

W. Wilson⁷⁶ has solved the problem by compressing the crude gas to an absolute pressure of about 3 atmospheres. By this means, the partial pressures of both the ammonia and the carbon dioxide are multiplied by three and their product by nine. Under these conditions, a large proportion of the ammonia can be made to produce ammonium bicarbonate. The procedure is to cool the gas and extract the tar

in the usual way and then distil into the gas the ammonia, free or total, from the virgin liquor, as in the semi-direct process of sulphate manufacture. The gas is then compressed and, after further removal of tar and oil, washed with a solution saturated with ammonium bicarbonate. Ammonia, carbon dioxide and water are extracted from the gas and ammonium bicarbonate deposits from the solution, from which it is separated and subsequently dried. Residual ammonia in the gas may then be removed in a small scrubber and the gas expanded to normal pressure and purified in the usual way.

This process has worked on a small scale without undue trouble. A great drawback is that it requires the compression of the whole of the crude gas, the cost of which may well greatly exceed that of the sulphuric acid used in sulphate manufacture. A further problem which might not be easy to solve on the large scale is the cooling which is required. Both the heat of compression and that of reaction must be effectively dissipated, since the temperature of the gas and the solution cannot be allowed to rise or the efficiency of conversion of ammonia to ammonium bicarbonate will be reduced.

If it were necessary in any case to compress the gas for some other reason, for example, for purification purposes, or if the gas were produced under pressure, some such process as Wilson's for producing ammonium bicarbonate might be very suitable. Under present conditions, however, there appears little chance of the process being a profitable one and it certainly seems more expensive to operate than other available processes.

THE STILL PROCESS

In this process,⁷⁷ the problem of obtaining sufficiently high concentrations of ammonia and carbon dioxide is solved by extracting these gases separately from the crude gas and bringing them into contact in a separate plant. The ammonia is extracted in the usual way and worked up by distillation into concentrated gas liquor. This passes to a washer or saturator fitted with a stirring device and cooling jacket, where it is treated with carbon dioxide. Absorption of carbon dioxide occurs, as in the Parrish process, with separation of ammonium bicarbonate, which is recovered, and production of a mother liquor which requires re-distillation to render it suitable for further use. The carbon dioxide, together with some hydrogen sulphide, is produced by the partial distillation, or decarbonation, of ammoniacal liquor. The latter is not, however, the same ammoniacal liquor from which the concentrated liquor is prepared but a special liquor which undergoes a cycle of processes. The first step in the cycle is the removal of carbon dioxide by heating the liquor to 90° C. or more under special conditions. The carbon dioxide enters the

saturator and is converted into bicarbonate; the residual liquor contains caustic ammonia, *i.e.*, ammonia not combined as carbonate, and this, after cooling, is used to extract carbon dioxide from the crude gas. This carbon dioxide is also removed by heating, and so the cycle proceeds.

The process is fairly simple and appears to be free from serious objections of a technical character. The extraction of the carbon dioxide from the gas should precede the extraction of the ammonia and would probably require a scrubber of similar size to the ammonia scrubbers. The decarbonation of the resulting liquor should present no difficulty since complete separation of the carbon dioxide and ammonia would not be necessary. The fact that two liquors instead of one require distillation would, however, almost double the normal distillation costs and the cost of efficiently cooling a relatively large volume of caustic ammonia solution from 90° C. to atmospheric temperature might be considerable. It is not known whether the process has been tried on a large scale.

THE KEY PROCESSES

The first of these processes^{78, 79} may be regarded as an attempt to obtain conditions in the crude gas stream similar to those prevailing in the Wilson process without resort to the costly compression process. Wilson increases the partial pressures of both the ammonia and carbon dioxide by compression; Key, by concentrating most of the ammonia and part of the carbon dioxide into a fraction of the crude gas, obtains a similar effect and ensures that the product $\frac{p_{\text{NH}_3}}{p_{\text{CO}_2}}$ greatly exceeds the equilibrium value at 20° C.

The crude gas stream is divided at the outlet of the condensers and the smaller fraction, the volume of which would depend on the carbon dioxide content of the gas, is subjected to a tar extraction process if necessary. The fractions later re-unite and pass to the ordinary ammonia scrubbers where they are freed from ammonia and a certain amount of carbon dioxide. The ammoniacal liquor is distilled in the usual way, at a rate equal to that of its production, and the gases from the still, which are refluxed so as to remove a considerable amount of the steam, are admixed with the smaller fraction of the crude gas. This now contains the same amount of ammonia as did originally the whole of the crude gas and the partial pressure of the ammonia is correspondingly increased. Owing to the carbon dioxide driven off from the ammoniacal liquor the carbon dioxide content of this gas fraction is also higher than normal. The product of the two is such that, when the gas is brought into intimate contact with a solution saturated with ammonium bicarbonate, absorption of ammonia and carbon dioxide takes place and crystallization of the salt occurs. The gas leaving the absorption vessel may be washed with ammoniacal liquor before rejoining the main gas stream.

An essential condition for the success of the process is that there should be an adequate amount of carbon dioxide available in the fraction of the crude gas which is enriched with ammonia. If the crude gas contains a relatively large percentage of carbon dioxide, only a small fraction will be treated for enrichment with ammonia and only a small scrubber will be required for the formation of bicarbonate. The process is thus especially suitable for vertical retort gas. With gas having a carbon dioxide content of 4 per cent., only about one-tenth of the gas would be required for enrichment purposes. On the other hand when the carbon dioxide content of the crude gas is only about 1.5 per cent. the whole of the gas must be enriched with ammonia; otherwise the amount of carbon dioxide available would not be sufficiently great. With gas of still lower carbon dioxide content the process would not operate, since under these conditions the ammonium salt formed would not be bicarbonate but a double salt containing normal carbonate.

The process has worked satisfactorily on a small scale but it is thought that, on the large scale, there would be difficulties in two directions:

- (1) The solution from which the bicarbonate separates would contain a large excess of ammonia and loss of this substance would be difficult to prevent.
- (2) The heat of formation of ammonium bicarbonate is considerable and it would be difficult to dissipate this without allowing the temperature of the solution to exceed about 20° C.

The second of the Key processes avoids these disadvantages by removing ammonia and a sufficiency of carbon dioxide from the crude gas before the bicarbonate reaction is allowed to take place. In this respect, it is similar to the Still process. An average ammoniacal liquor contains approximately the amount of carbon dioxide necessary to form bicarbonate with one-half of the free ammonia present. The first stage of the process consists in obtaining this carbon dioxide in the gaseous form mixed with one-half of the free ammonia and allowing this mixture to form ammonium bicarbonate whilst the remaining ammonia is used to extract a further supply of carbon dioxide from the crude gas. n-

It is known to be possible to remove almost the whole of the carbon dioxide from a crude liquor without loss of more than a trace of ammonia. This is actually effected in the decarbonation process which precedes distillation in the preparation of concentrated ammonia liquor. There must therefore be some point in the distillation process where the liquor has lost the whole of its carbon dioxide and one-half of its free ammonia. In the present scheme, distillation is interrupted at this point and the liquor immediately proceeds to another still, conveniently situated below the first still. The

carbon dioxide and ammonia evolved up to this point are in approximately the correct ratio to form bicarbonate and they are allowed to do so either with or without preliminary removal of excess steam. The formation of bicarbonate is effected by washing the still gases with a solution already saturated with ammonium bicarbonate. Absorption of both ammonia and carbon dioxide is fairly rapid and complete even at temperatures of the order of 40°C ., so that cooling of the solution presents no difficulties. The solution itself provides a sort of reservoir which corrects any irregularities in the composition of the gases leaving the still. It contains little excess ammonia and may therefore be easily handled without loss of this substance.

The partially distilled liquor from the first still contains about one-half of its original free ammonia with but little or no carbon dioxide. This ammonia is driven off in the second still and collected as a relatively concentrated solution having a strength of, say, 5 to 10 per cent. After cooling, this solution is fed to a scrubber situated in the crude gas stream between the condensers and the ammonia scrubbers. This scrubber would usually be small and only a fraction of the crude gas would be passed through it. In this scrubber the ammonia solution extracts carbon dioxide from the crude gas until the ratio of ammonia to carbon dioxide in the solution is approximately the same as in crude ammoniacal liquor. The solution is then returned to the liquor well or direct to the first still where it re-enters the process. Thus the only outlet for ammonia is as bicarbonate, which should be in a particularly pure and stable form.

This process has worked well in the laboratory but has not been tried out on a large scale. The various stages of the process are, however, well understood and there is no apparent reason why the process should not be made to work successfully.

RECOVERY OF FIXED AMMONIA

It should be noted that any of the processes described in this Section may be operated for the recovery of only the free ammonia or of both the free and the fixed ammonia. For the recovery of the fixed ammonia it would be necessary to add lime during the distillation and to make slight modifications in the working conditions so as to ensure the process working at its greatest efficiency.

COSTS

Without experience on a large scale, it is not possible to assess accurately the costs of ammonium bicarbonate production. A study of the various stages involved leads to the conclusion that, in many circumstances, the cost should be less than that of the manufacture of ammonium sulphate from the same source. As a first approximation, it may be

said that the cost of bicarbonate production by the best of the proposed processes should be smaller than the cost of sulphate production by an amount rather less than the cost of sulphuric acid in the latter process.

It may be concluded that if, in the future, circumstances develop in which it is desirable that gas works ammonia should be recovered as ammonium bicarbonate, processes could readily be made available for its economic production. It is possible that, even at the present time, some individual Gas Undertaking might find it advantageous to produce ammonium bicarbonate and develop a specialized market for it. Such a development would provide information valuable to the Gas Industry as a whole.

XIII THE MANUFACTURE OF CONCENTRATED GAS LIQUOR

It is now apparent that no great benefit is likely to accrue to the Gas Industry by making any change in the form in which its ammonia is recovered and finally sold. It has also been shown that no process of ammonium sulphate manufacture is, at the moment, in a position to compete successfully with the established method of neutralizing ammonia with sulphuric acid. At the present time, therefore, any improvement must be in the present process of sulphate production.

Some possible economies, such as those effected by increasing the strength of crude ammoniacal liquor, have already been mentioned and the way in which they can be accomplished has been described. These economies apply to all Gas Works, whatever their size. Other economies, however, for example in the cost of sulphuric acid and in overhead charges and labour costs, cannot well be made on small Works. They can be made, however, by changing over from small-scale operation to large-scale working. On large-scale plants capital and labour costs are usually smaller per ton of product than on small-scale plants. In addition, Works which operate large-scale sulphate plants may well be able to work sulphuric acid plants and be able to supply this product to the sulphate plants at a price considerably lower than that at which it could be purchased elsewhere. The centralization of sulphate of ammonia production must therefore be considered as a method of solving the ammonia problem. The central sulphate works could be either a large Gas Works which could receive the ammonia from surrounding smaller Works for working up or a central chemical works which could deal with all the ammonia from Gas Works in the vicinity.

Clearly the success of such a method of operation would depend almost entirely on the availability of a cheap method of transport of the ammonia from the outlying to the central works. Crude ammoniacal liquor is only a very dilute ammonia solution and the conveyance of the whole of this liquor over more than a small distance would entail a prohibitive expense. For instance, a charge of 4s. per ton for the transport of a 10 oz. liquor works out at £2 12s. per ton of sulphate, which is one-third of the present retail price and more than one-half of what the maximum total cost of sulphate making should be if a profit is to be made at the present market price. In addition, the carriage of all the ammoniacal liquor to a central works for treatment would result in the production of all the effluent liquor from a number of Gas Works at one point and render the disposal of the latter very difficult. It is, in most cases, highly desirable that the effluent should be disposed of over as wide an area as possible so

that the load on sewage purification plants shall be as uniform as possible. Hence it is usually preferable to dispose of the great bulk of the effluent direct from the Gas Works in which the ammoniacal liquor is produced.

Some method must therefore be adopted of concentrating the ammonia into a much smaller volume before it is transported to a central works. Such a method should be capable of being easily operated, should be economical on a comparatively small scale and should produce a concentrated form of ammonia which is easily handled and transported. These requirements are, to a large extent, satisfied by the modern automatic concentrated gas liquor plants.

Concentrated gas liquor must not be confused with what is known as concentrated ammonia liquor. The latter is prepared from gas liquor and consists of a strong solution of ammonia contaminated with as little hydrogen sulphide and carbon dioxide as possible. Concentrated gas liquor is also a strong solution of ammonia but the presence of quite large, but not too large, proportions of carbon dioxide and hydrogen sulphide is not a disadvantage, but rather desirable. It is, in consequence, more simply prepared than concentrated ammonia liquor.

Concentrated gas liquor plants may generally be divided into two types:

- (i) Those which are intended primarily for the preparation of liquor containing 15 to 18 per cent. of ammonia by weight.
- (ii) Those designed to produce liquor of 20 to 24 per cent. strength.

The latter are rather more complicated and expensive to operate but, in some cases, the saving in transport costs may make them an economic proposition. This classification of the types of plant according to the strength of liquor produced is not a hard and fast one; it is possible with some ammoniacal liquors, for instance, to produce a concentrated liquor of 20 per cent. strength with a plant of the first type. The reason for this will become apparent later.

THE SIMPLE TYPE OF CONCENTRATED GAS LIQUOR PLANT

A plant of the first type has been described by R. J. Philp.⁶⁰ It consists essentially of a still, a condenser, heat interchanger and the necessary automatic controls. The arrangement is shown in diagrammatic form in Figure 5. The still is of the continuous multi-stage type and, in several cases, a still from a disused sulphate of ammonia plant has been used. It is not the general practice to recover the fixed ammonia in these plants, but a liming section could be incorporated if desired. The preheater and condenser are usually of the double tubular type, the cooling water or the crude liquor passing through the inner tube and the gases from the still through the

annulus between the inner and outer tubes or *vice-versa*. The automatic control serves to regulate the supply of crude liquor and steam, the strength of product and to provide for the plant being shut down in the case of accidentally blocked pipes.

The crude ammoniacal liquor either flows by gravity, or is pumped, from a storage tank through the preheater to the still. In the preheater it is heated by the gases leaving the

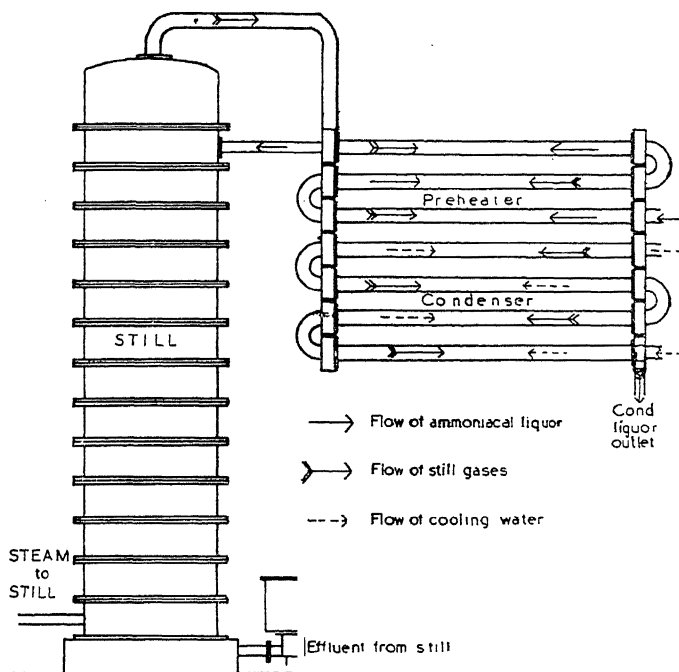


FIGURE 5.—Simple Type of Plant for the Manufacture of Concentrated Gas Liquors.

still. The degree of preheating may be important. In order that the minimum of steam should be used for distillation, it is desirable that a liquor as hot as possible should enter the still; on the other hand, if it is necessary that some reflux action should take place in the still itself so as to produce the desired strength of product, the liquor entering the still should be cool enough to allow this to occur. In these cases, there is therefore a critical temperature above which the ingoing liquor should not be preheated. This critical point is not likely to be exceeded with the simple type of concentrated

liquor plant unless a very weak crude liquor is being dealt with. Distillation is effected by the agency of a controlled quantity of steam, and the effluent from the still, which should be almost free from free ammonia, is disposed of in any suitable manner. The gases leave the still at a controlled temperature and are cooled first by crude liquor in the preheater and then by water in the condenser. The condensed liquor flows to the concentrated liquor storage tank and any uncondensed gases are freed from ammonia, hydrogen sulphide and hydrogen cyanide, before being allowed to escape to atmosphere. The scrubber in which the ammonia is removed is commonly situated at the outlet of the storage tank but it is doubtful if this is the best location.

A number of plants of this type have been erected in different parts of the country and, apart from minor troubles, are working well. In many cases ammonia recovery now shows a slight profit. The chief trouble experienced is an occasional blockage in the condenser or in the pipe joining it to the storage tank, a compound of carbon dioxide, ammonia and water being deposited. It has been shown¹ that this compound is deposited from the gaseous phase and that its formation can be avoided by keeping the surfaces of the condenser and of the pipes which follow it wet with concentrated liquor. This procedure would entail some rearrangement and, possibly, a re-design of the cooler end of the condenser. Blockages can, however, be minimized, and in some cases avoided altogether, by separating the concentrated liquor and the uncondensed gases immediately they leave the condenser, allowing the former to flow to storage through a pipe which is kept full and passing the latter, accompanied by a little steam if necessary, direct to the scrubber for the removal of ammonia.

COMPOSITION OF CONCENTRATED GAS LIQUOR

The ammonia content of the concentrated liquor depends on the amount of steam in the gases leaving the still, which is regulated by the temperature of the still gases, and on the efficiency of the removal of the ammonia from the gaseous phase. The extent to which other substances, notably carbon dioxide and hydrogen sulphide, occur in the concentrated liquor depends largely on their concentration in the original ammoniacal liquor and on the conditions of operation of the condenser. The importance of the latter is best shown by a study of the process in this part of the plant.

The extent to which the steam condenses is largely governed by the temperature to which the gases are lowered and it can be said that equilibrium between water in the vapour and liquid states is attained instantaneously at all temperatures. Water, once it has begun to separate, commences to take the other gases, notably ammonia and carbon dioxide, into solu-

tion, but the rates of absorption of the two gases differ. The chief factors governing the rate of absorption of ammonia, apart from a constant which takes into account the specific velocity of the process, are:

- (1) The ammonia concentration in the gaseous phase. Other things being equal, the velocity of absorption of ammonia by an aqueous solution will generally be directly proportional to this.
- (2) The concentration of uncombined ammonia in the solution. The greater this is, the slower will be the absorption of further quantities of ammonia.
- (3) The temperature. The lower the temperature the more rapid will be the absorption in most cases since the solubility of the ammonia is thereby increased and the concentration of the uncombined ammonia in the solution becomes further removed from the saturation value.

The rate of absorption of carbon dioxide by an ammonia solution is also governed by a specific velocity constant and is, in addition, controlled by the following factors:

- (a) The carbon dioxide concentration of the gas. The velocity of absorption will be directly proportional to this factor.
- (b) The concentration of uncombined ammonia in solution. Absorption of carbon dioxide in the circumstances under consideration converts the uncombined ammonia into ammonium carbonate. The greater the uncombined ammonia concentration, therefore, the greater is the velocity of carbon dioxide absorption. This effect should be contrasted with the effect of uncombined ammonia on ammonia absorption.
- (c) The temperature. Again, a lower temperature will favour absorption since the partial pressure exerted by the carbon dioxide in the solution will be decreased.

It will now be evident that, at any stated temperature, the velocity of ammonia absorption will at first be high, and that it will fall as the ammonia content of the solution increases and that of the gas decreases. The velocity of carbon dioxide absorption, on the other hand, will be low at first owing to the small uncombined ammonia content of the solution, but will increase later owing to the progressive increase of the latter factor. Finally, the velocity will fall as absorption approaches completion. Thus, in general and within limits, the lower the efficiency of ammonia absorption the greater is the ratio of ammonia to carbon dioxide in the product. The importance of this ratio will become apparent later.

Liquors prepared in the simple type of concentrated liquor plant where the efficiency of ammonia absorption in the condensers approaches 100 per cent. have an NH_3/CO_2 ratio not

much greater than that of the original ammoniacal liquor. A concentrated liquor containing 15 per cent. of ammonia would generally contain about 18 per cent. of carbon dioxide.

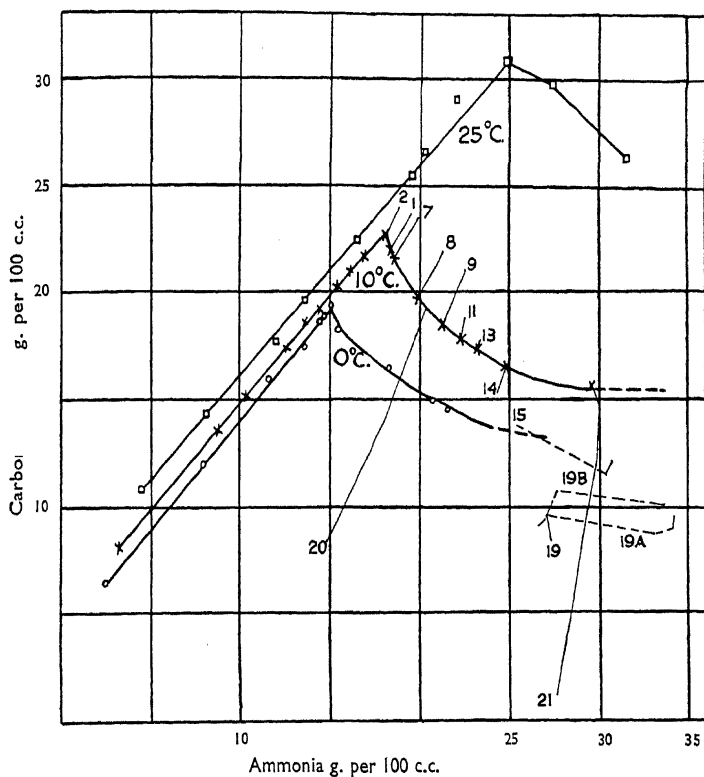
Concentrated liquor plants of this type usually produce a liquor the $\text{NH}_3/\text{H}_2\text{S}$ ratio of which is very nearly the same as that of the ammoniacal liquor. On the average, a liquor of the above composition would contain about 2 per cent. of hydrogen sulphide.

Concentrated liquor also contains smaller quantities of other substances which are removed from ammoniacal liquor by steam distillation. Of these, phenols are of most importance, but bases and neutral oils are also present. Generally, the concentration of phenols in a distillate from ammoniacal liquor is approximately twice that in the liquor. A phenol content of about 0.4 to 0.6 g. per 100 c.c. is therefore to be expected in the average concentrated liquor. However, the solubility of phenols in concentrated liquor is much smaller than in water and it frequently happens that almost one-half the amount of the phenols separates from the cooled concentrated liquor as a light oil, so that the amount of phenols in solution may not exceed about 0.3 g. per 100 c.c. The quantity of oil separating would be of the order of 0.5 gal. per ton of concentrated liquor.

THE CRYSTALLIZATION OF CONCENTRATED GAS LIQUOR

Concentrated liquor prepared in a plant of the simple type from an ammoniacal liquor of average composition is liable to deposit crystals in cold weather if the ammonia content exceeds 15 to 18 per cent. by weight. It is important that crystallization should not occur to such an extent that storage or transportation is hampered. It is desirable, however, if transport costs are to be kept to a minimum, that the strength of the liquor should be as high as possible. In order that both these objectives may be attained, knowledge of the factors governing the crystallization of concentrated liquor is clearly necessary. The results of an investigation on this subject have been published.⁵²

It has been found that, depending on its composition, concentrated liquor may deposit crystals of ammonium bicarbonate, normal ammonium carbonate or a double salt composed of two molecules of ammonium bicarbonate and one of normal ammonium carbonate. It has also been shown that, particularly with liquors which deposit crystals of the normal carbonate, there is present in the solution ammonium carbamate ($\text{NH}_2\text{CO}_2\text{NH}_2$). In liquors containing a large excess of ammonia the carbamate actually predominates. Ammonium carbamate is, in fact, produced from and converted into ammonium carbonate by a reversible reaction. Any crystals of ammonium carbonate which may be deposited will, of course, be in equilibrium with the ammonium carbonate in solution, but, if the latter is not also in equilibrium with



Thick lines connect final equilibrium values.

Thick dotted lines are extrapolations.

Thin lines refer to 10° C. and connect intermediate compositions.

Thin dotted lines connect determinations between which ammonia gas or ammonium bicarbonate had been added to the solutions.

FIGURE 6.—Compositions of Concentrated Gas Liquors, free from Sulphide, in Equilibrium with Crystals at Temperatures of 0°, 10° and 25° C.

ammonium carbamate, the crystallization point will bear no quantitative relationship to the total ammonia and carbon dioxide contents of the liquor. There is thus the possibility of liquors of the same apparent composition crystallizing or not crystallizing according to the relative concentrations of carbonate and carbamate. This possibility might produce rather disturbing results in practice were it not that the carbonate-carbamate equilibrium appears usually to be displaced, if at all, towards the carbamate side. It is thus more likely that liquors will remain liquid when expected to crystallize than that the reverse will happen.

The carbonate-carbamate reaction is very slow at air temperatures and takes days or weeks to reach equilibrium. When this is attained, however, and the liquor is in contact with crystals, the composition of the solution becomes fixed and represents the final composition of a saturated solution. Series of determinations of such final compositions at different temperatures were made and the results are reproduced in graphical form in Figure 6. Ammonia concentration is plotted against carbon dioxide concentration and curves show the composition of liquors, free from sulphide, which are in complete equilibrium with a solid phase. Liquors having compositions which come below the curves will, normally, not deposit crystals at the temperatures for which the curves are drawn. Liquors having compositions which come above the curves may or may not deposit crystals immediately at the temperature in question (depending on the relationship between carbonate and carbamate) but will ultimately crystallize if allowed to remain for a sufficiently long time at that temperature.

The first part of each curve approximates to a straight line of positive slope. As the ammonia content of the solution rises so does the carbon dioxide content. In this section, the crystals which are in equilibrium with the solution are of ammonium bicarbonate over most of the range, but the double carbonate constitutes the solid phase at the highest concentrations. The second portion of each curve has a negative slope and the crystals with which the solutions are in equilibrium are the normal ammonium carbonate. In this section, increasing ammonia content is accompanied by decreasing carbon dioxide content.

It should be noted that the curves in Figure 6 refer to liquors from which hydrogen sulphide is absent and that the influence of this substance on crystallization is not accurately known. It has, however, been ascertained that, in presence of hydrogen sulphide, the carbon dioxide content of a liquor in equilibrium with crystals is reduced. As a rough approximation, 1 per cent. of hydrogen sulphide can be taken as replacing 0.5 per cent. of carbon dioxide in equilibrium mixtures.

The change in direction of the solubility curve for 10° C..

which may be taken as an average air temperature, occurs at a concentration of 18 per cent. of NH_3 by volume, equivalent to 15.8 per cent. by weight. When the ammonia content of a liquor rises above this figure, the carbon dioxide content must be reduced and the NH_3/CO_2 ratio greatly increased if deposition of crystals is to be avoided at this temperature. This provides the explanation of the frequent failure to produce liquors more concentrated than this in simple concentrated liquor plants without trouble due to crystallization. As such plants are normally operated, if the ammonia content of the liquor is increased by adjustment of the still head temperature, the carbon dioxide content is also increased, whereas to avoid crystallization it should be decreased. In order to produce liquors containing much more ammonia than 15 to 18 per cent., it is therefore necessary to adopt measures to reduce the carbon dioxide content. This can be achieved in two ways: (a) by modifying the composition of the liquor before distillation and (b) by modifying the conditions of condensation of the gases from the still. The second method is capable of limited application only.

CONCENTRATED LIQUOR PLANTS INCORPORATING PARTIAL DECARBONATION

In the preparation of concentrated ammonia liquor, *i.e.*, a liquor containing a large percentage of ammonia but as little carbon dioxide as possible, the carbon dioxide contained in the crude ammoniacal liquor is removed in a decarbonating still before the liquor proceeds to the still proper. The steam supplied to the decarbonating still is sufficient to remove the carbon dioxide, which is more volatile than ammonia, but removes very little of the ammonia. Since the adoption of this process results in the production of a concentrated liquor almost free from carbon dioxide, the removal of a portion only of the carbon dioxide from ammoniacal liquor before distillation must result in the production of a concentrated liquor containing a smaller quantity of carbon dioxide than is obtained by simple distillation. The details of the apparatus in which partial decarbonation is affected vary in different types of plant. In one type⁸³ a portion of the carbon dioxide is removed in a small multi-stage still through which a strictly limited amount of steam passes. Preheated crude liquor is fed into this still, the point of entrance being below the top. Some carbon dioxide and a little ammonia are removed from the liquor by the steam, but escape of ammonia from the system is prevented by the introduction of a stream of cold crude liquor to the top sections of this still. The decarbonated liquor then flows to the ordinary ammonia still. In another type,⁸⁴ preheated liquor, together with a certain amount of steam, is introduced into the decarbonating vessel which consists of a splash chamber surmounted by a reflux

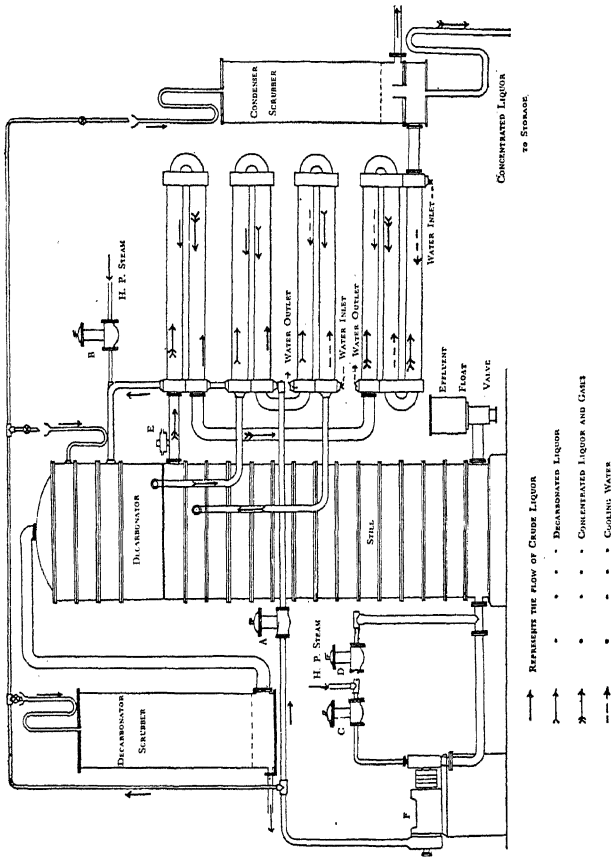
system. Carbon dioxide and some ammonia are removed in the splash chamber, part of the ammonia is retained by cold liquor flowing down the reflux sections and the rest is extracted in an external scrubber.

In order to produce a concentrated liquor containing 20 or more per cent. of ammonia, it is, in most cases, necessary that the gases leaving the still should be refluxed to some extent so as to limit the amount of outgoing steam. In the type of plant first mentioned, this is accomplished by use of a reflux condenser, which also serves as a preheater, situated before the main condenser. In the other type of plant, the refluxing takes place in the still itself and, for this purpose, the liquor entering must be cooled to a sufficiently low temperature.

A series of tests on a plant of the second type has been carried out on behalf of The Institution of Gas Engineers.⁵⁵ The arrangement of the plant is shown in diagrammatic form in Figure 7. Ammoniacal liquor is pumped by a turbine pump F through heat interchangers, where it is preheated first with liquor from the decarbonator and secondly with gases leaving the still, to the decarbonator, which it enters together with a supply of steam. Gases from the decarbonator are scrubbed in the "decarbonator scrubber." The partially decarbonated liquor is again passed through heat interchangers, where it is cooled by ingoing crude liquor and by water, prior to entering the still proper. The gases from the still are cooled first by liquor on its way to the decarbonator and later by water. Any uncondensed gases are finally dealt with in the "condenser scrubber." The concentrated liquor passes through a liquor seal to storage. Subsidiary supplies of crude ammoniacal liquor from the pump are fed to the two scrubbers and to the reflux sections of the decarbonator.

The primary purpose of the decarbonator is to diminish the amount of carbon dioxide in the gases leaving the still proper. The decarbonator is not intended to remove the whole of the carbon dioxide, for the product would then be concentrated ammonia liquor. This would not be so easy to handle on account of its higher vapour pressure of ammonia and it would have a specific gravity less than unity. A density greater than that of water is necessary where transport by rail is involved, in order that advantage of a special scale of charges may be gained.

The diminution in the amount of carbon dioxide in the gases leaving the still or, as more commonly expressed, the rise in the NH_3/CO_2 ratio, causes this ratio in the concentrated liquor to be augmented and thereby enables liquor of increased strength to be prepared without risk of crystal formation under normal conditions. In the particular circumstances of the test, an increase of about 40 per cent. in the NH_3/CO_2 ratio in the still gases caused an increase of about



- A. Automatic liquor control valve.
- B. Automatic control valve for steam to decarbonator.
- C. Automatic control valve for steam to turbine.
- D. Automatic control valve for steam to base of still.
- E. Thermo-relay.

FIGURE 7.—Diagrammatic Representation of Coventry Concentrated Liquor Plant.

15 per cent. in the corresponding ratio in the final concentrated liquor. The result was that, with the decarbonator in operation, the ammonia content of the final liquor could be increased by 2 to 3 g. per 100 c.c. without crystallization troubles. This is not necessarily quantitatively true for all conditions but it may be said, with some degree of confidence, that the increase in the NH_3/CO_2 ratio in the concentrated liquor will generally not be so great as the increase in the same ratio in the gases leaving the still.

THE EFFECT OF THE EFFICIENCY OF CONDENSATION ON THE COMPOSITION OF THE CONCENTRATED LIQUOR

It has been previously pointed out that condensation of water vapour occurs before solution of ammonia. It would therefore be expected that the lower the efficiency of ammonia solution the lower would be the strength of the product. This is, in fact, the case but the effect can be to a large

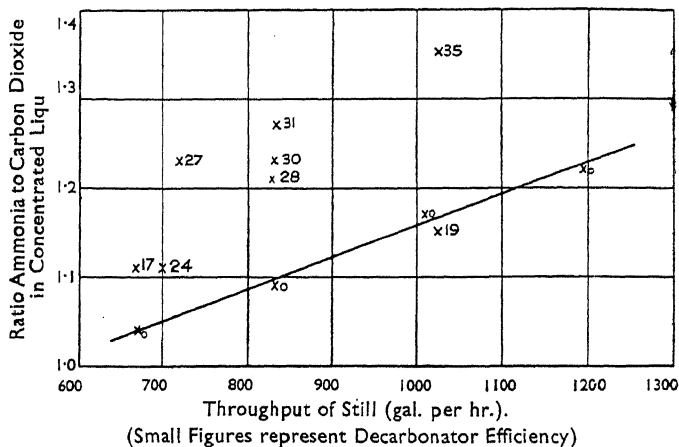


FIGURE 8.—Coventry Concentrated Liquor Plant; Throughput of Still Plotted against Ratio of Ammonia to Carbon Dioxide in Product.

extent counteracted by lowering the temperature of the gases leaving the still. This lowers their water content and by this means the ammonia content of the concentrated liquor can, between certain limits, be made independent of the efficiency with which the ammonia is removed from the gaseous phase.

Of more importance, because it is not so readily controlled, is the NH_3/CO_2 ratio in the final liquor. This is affected by several factors apart from the degree of decarbonation but the influence of efficiency of solution of ammonia is clearly shown in Figure 8. This is taken from the report of the test

previously referred to and the NH_3/CO_2 ratio of the concentrated liquor is plotted against the throughput of the plant. The straight line, drawn connecting those points representing tests in which the decarbonator was not in operation, clearly shows that an increased throughput was accompanied by an increased NH_3/CO_2 ratio in the concentrated liquor. Since, other things being equal, an increased throughput must mean a decreased time of contact in the condensers and a decreased efficiency of solution of ammonia, it follows that the NH_3/CO_2 ratio can be increased by decreasing the efficiency of condensation. This also follows from the general principles of condensation enunciated on p. 117; it was there shown that the ammonia tended to condense towards the beginning of the process and the carbon dioxide towards the end.

It will be seen, therefore, that a second method, and one which is quite effective within certain limits, of producing a stronger liquor without possibility of crystallization is to decrease the efficiency of ammonia solution by increasing the throughput of the plant. The same desirable effect would not necessarily follow if the condensation efficiency were reduced by some other method, for example, by cutting down the water supply to the condensers. It might be thought that this method of increasing the NH_3/CO_2 ratio in the product might result in increased costs, since the undissolved ammonia must be recovered and redistilled. But this does not occur to any appreciable extent. By recovering the uncondensed ammonia by washing with crude liquor the volume of liquor to be distilled is not increased. Additional steam is therefore only necessary for the re-expulsion of the ammonia and carbon dioxide. On the other hand, it is necessary that a smaller amount of steam should leave the still with the still gases since the object of the adoption of this procedure is to enable a stronger concentrated liquor to be prepared. Calculation shows that these two items almost exactly balance, so that decreasing the condenser efficiency in this way may be regarded as a method of increasing the possible strength of the final crystal-free liquor without cost. There is a definite limit, however, beyond which this process cannot be carried. It is reached when the amount of steam leaving the still is insufficient to ensure efficient stripping of the ammoniacal liquor.

RECOVERY OF FIXED AMMONIA AS CONCENTRATED LIQUOR

Most of the concentrated liquor plants which have been erected during the past few years have been designed for the recovery of free ammonia only. It is possible, however, to incorporate liming apparatus for the recovery of the total ammonia whilst still retaining the advantages of automatic control. It is not proposed to discuss here the economics of fixed ammonia recovery, but one point may be mentioned which would usually escape notice and which is in its favour.

When fixed ammonia is driven off from a liquor it is not accompanied in the vapour stage by carbon dioxide or hydrogen sulphide. Hence, when the gases from the "fixed" still are added to those from the "free" still, the ratio NH_3/CO_2 must be increased considerably. The same ratio in the concentrated liquor must also be increased and it would be possible to prepare a stronger liquor without danger of crystallization troubles. Recovery of fixed ammonia has therefore the same result in this direction as the operation of a partial decarbonator, and the financial value of the effect should be credited to the fixed ammonia recovery process.

ECONOMICS OF CONCENTRATED LIQUOR MANUFACTURE

The capital cost of a concentrated liquor plant, per ton of concentrated liquor produced per day, will vary with the size of the plant, and the interest and depreciation charges per unit of ammonia produced will be subject to similar variations. These may range from several pence per unit of ammonia (one-hundredth of a ton) for a small plant to less than one penny for a large one, and it would therefore be misleading to give an average figure. Labour, supervision and maintenance charges should be low for all plants.

Apart from these charges the cost of producing concentrated liquor depends more than anything else on the amount and the cost of the steam used. This should not vary much with the size of plant, provided this is efficiently operated. Some Works might have available sufficient surplus steam which could be used for the distillation, the cost of which would in consequence be almost negligible. Other works, requiring to generate steam specially for the distillation, would be interested in cutting down steam consumption to the lowest possible point.

In order to estimate the amount of steam required under different conditions it is necessary to make a heat balance, taking into account the following items:

(a) Heat supplied to plant, contained in

- (1) Liquor passing to decarbonator (if one is used);
- (2) Liquor passing to reflux sections of decarbonator (if used);
- (3) Liquor passing to still itself, with due regard to the fact that the liquor may be diluted slightly by steam in the decarbonator;
- (4) Steam supplied.

(b) Heat leaving or absorbed in plant, contained in or represented by

- (1) Liquor leaving decarbonator, with due regard to dilution;
- (2) Liquor leaving still, with due regard to dilution;

- (3) Heat required to dissociate the ammonium carbonate in the liquor (=833 B.Th.U. per lb. of NH_3), to volatilize ammonia (=893 B.Th.U. per lb. of NH_3) and to volatilize carbon dioxide (=240 B.Th.U. per lb. of CO_2);
- (4) Heat required to evaporate water leaving system, mainly at the still head, to provide water for the concentrated liquor (including any reflux condensate returned to the still), and partly to saturate the gases which leave the decarbonator and the condenser uncondensed;
- (5) Heat lost by radiation, used in pumping and lost by accidental means.

If a reasonable value for the last item be assumed, the amount of steam required may be calculated from a knowledge of the quantities and temperatures concerned. The figures given in Table 20 have been calculated for a set of conditions which need not be accurately specified here. They relate to a plant having the splash chamber type of decarbonator and in which refluxing takes place within the still itself. Figures for steam consumption are given for liquors of various strengths and with and without the decarbonator in operation. The figures do not necessarily represent ideal conditions but serve to draw attention to the important factors governing steam consumption.

TABLE 20.—*Steam Consumption in Concentrated Liquor Production*

Ammonia in work: crude liquor, g. per 100 c.c.	0.75	1.5	3.0
1	2	3	4
Steam used, lb. per 100 lb. of liquor:			
Without decarbonator	17.0	22.0	32.0
With decarbonator	21.3	26.6	37.0
Steam used, lb. per unit of NH_3 :			
Without decarbonator	522	338	247
With decarbonator	638	409	284
Cost of steam at 5s. per ton, pence per unit of NH_3 :			
Without decarbonator	14.0	9.1	6.6
With decarbonator	17.6	11.0	7.6
Cost of steam at 1s. 6d. per ton (waste heat steam), pence per unit of NH_3 :			
Without decarbonator	4.2	2.7	2.0
With decarbonator	5.3	3.3	2.3
Cost of transport at 10s. per ton of liquor, pence per unit of NH_3 :			
Without decarbonator		6.5	
With decarbonator		6.0	
Cost of transport at 3s. per ton of liquor, pence per unit of NH_3 :			
Without decarbonator		1.95	
With decarbonator		8.1	

The chief of these is the strength of the crude ammoniacal liquor. The weaker the liquor the greater are the amount and the cost of the steam necessary to produce one unit of ammonia as concentrated liquor. The desirability of producing as strong a crude liquor as possible is therefore apparent. A further point is that the extra steam required by the decarbonator, if one is used, is proportional to the volume of liquor treated and independent of its ammonia content. To reduce decarbonation costs it is therefore necessary to reduce the volume of liquor or, in other words, to increase its strength. In Table 20 it is assumed that, both with and without the decarbonator, the liquor of greatest possible strength compatible with absence of crystal formation at 10°C . is made. It will be seen that the advantage of decarbonation, so far as it reduces the transport costs of the product, is small. For decarbonation to be an economic proposition, the necessary conditions are a strong crude ammoniacal liquor, a cheap source of steam and a high cost of transport. Otherwise the decarbonator will result in increased costs, though these may be offset by other advantages of partial decarbonation, the chief being a reduction in the likelihood of blockages occurring in the condenser.

By suitable adjustment in design it should be possible without extra cost to obtain a greater degree of decarbonation than has hitherto been aimed at. The extra steam necessitated by a decarbonator serves the purpose of heating the liquor to the decarbonating temperature and not of expelling the carbon dioxide from solution. A temperature of two or three degrees above, say, 90°C . would greatly increase the amount of carbon dioxide removed without requiring an appreciably greater amount of steam. It is easy to visualize the occurrence of decarbonation to the extent of 70 per cent. or more, resulting in a NH_3/CO_2 ratio in the concentrated liquor of at least 2.0. With this ratio, a liquor containing as much as 30 per cent. of ammonia could be prepared without danger of crystallization troubles at 10°C . Although the cost of transport would be much reduced in consequence, the production of such a liquor would have disadvantages in that the liquor would be objectionable to handle and, owing to its high partial pressure of ammonia, accidental losses of this substance would be greater.

HYDROGEN SULPHIDE

It should be mentioned that the ratio of ammonia to hydrogen sulphide in concentrated liquor is approximately the same as in the still gases, and that it is impossible to effect partial separation of these two substances by controlling the conditions of condensation. In the decarbonator a rather greater proportion of hydrogen sulphide than of carbon dioxide appears to be removed.

COLOUR IN CONCENTRATED GAS LIQUOR

In some cases concentrated gas liquor may be liable to develop some discoloration owing to traces of colour-producing bodies being carried over from the still. This may reduce the value of the liquor if it is to be used for certain purposes other than ammonium sulphate manufacture. Such discoloration may be eliminated by methods which prevent the occurrence of colour-producing substances, chiefly higher tar acids, in the ammoniacal liquor (see pp. 70-72). It might be sufficiently reduced by diverting from the concentrated liquor plant the first few gallons of virgin liquor condensed, which contain the larger proportion of higher tar acids, and disposing of this in some other way, or by suitable control of conditions in the concentrated liquor still and condenser.

CONCLUSION

It appears that the production of concentrated gas liquor in automatic plants and the sale of the product to a central Works would constitute the best solution of the ammonia problem in the case of a large number of Gas Undertakings. In many cases, the process has already been adopted with every success. It is not to be expected that the process will yield large profits but, with due regard to its ease and cheapness of operation and to the fact that it is the best single known process for fitting ammoniacal liquor for subsequent disposal, it is to be recommended.

APPENDIX 1

METHODS OF ANALYSIS OF AMMONIACAL AND SPENT LIQUORS

The methods which have been used in connexion with the data given in the text and which are recommended for the analysis of ammoniacal and spent liquors are substantially those described in the Technical Index to the Alkali Reports, 1894-1917, and in the 64th Report on Alkali etc. Works, though slight modifications have been found desirable in a few cases. Those portions of the following descriptions which are taken verbatim from one or other of the above reports are enclosed in inverted commas. Methods of analysis developed since the publication of these reports may give more reliable results, but experience has shown that the methods given below are sufficiently accurate for most purposes.

Free Ammonia

Ammoniacal Liquor.—"By distillation: 10 c.c. of liquor (more, if weak) are diluted to about 300 c.c. in a round bottomed flask connected through catch bulb to Liebig condenser and receiver with inlet tube sealed in excess of $N/2 H_2SO_4$ ". Provided the receiver is fairly large and has a narrow mouth no acid catch is necessary. "200 c.c. of the solution are distilled over and the excess acid in the receiver is titrated with $N/2 Na_2CO_3$ " or NaOH. "On further distillation certain liquors continue to evolve traces of ammonia. The presence of this ammonia is attributed to the slow decomposition of fixed salts of ammonia, or possibly of nitrogenous bodies, and the distillation for free ammonia is not continued beyond 200 c.c."

Spent Liquor.—The same method is used but, for accurate results, it is necessary to use 50 c.c. or more of liquor.

Fixed Ammonia

Ammoniacal Liquor.—"By distillation: Add 150 c.c. of a 2 per cent. caustic soda solution to the residual liquor in flask above and distil off 200 c.c. as before."

Spent Liquor.—The determination of fixed ammonia may be carried out on the residue from the free ammonia determination, but more caustic soda and standard $N/2$ acid will be required on account of the greater volume of liquor employed.

$$NH_3, \text{ in g. per } 100 \text{ c.c.} = \frac{0.85 \times \text{c.c. } N/}{\text{c.c. liquor taken}}$$

Cyanide

Ammoniacal Liquor.—"Feld's method: 50 c.c. of liquor are diluted and distilled with excess of lead nitrate solution into 20 c.c. of $N/2$ caustic soda. The distillate is titrated with $N/10 AgNO_3$, after the addition of a crystal of potassium

iodide." The end point, shown by the solution becoming opalescent, is not always very satisfactory but is usually sufficiently so for ordinary purposes.

$$\text{HCN, in g. per 100 c.c.} = \frac{0.54 \times \text{c.c. N/10 Ag}}{\text{c.c. liquor taken}}$$

Spent Liquor.—Cyanide is absent.

Thiosulphate

Ammoniacal Liquor.—Sulphide is first removed from 10 or 25 c.c. of the liquor either by running the liquor on to excess of lead carbonate, stirring well and filtering, or by mere boiling and then treating the liquor as in the method for spent liquor described below.

Spent Liquor.—10 or 25 c.c. of liquor are diluted to about 150 c.c. with distilled water containing 20 to 30 c.c. of 25 per cent. sulphuric acid and rather more than sufficient N/10 iodine solution to react with the thiosulphate. The excess of iodine is titrated with N/10 sodium thiosulphate using starch as indicator.

$$\text{Thiosulphate, as S in g. per 100 c.c.} = \frac{0.64 \times \text{c.c. N/10 I}_2}{\text{c.c. liquor taken}}$$

Sulphide

Ammoniacal Liquor.—10 c.c. of the liquor are run into 150 c.c. of distilled water acidified with 20 to 30 c.c. of 25 per cent. sulphuric acid and containing an excess of N/10 iodine solution. The excess of iodine is titrated with sodium thiosulphate. The total iodine consumption thus determined, less that consumed by thiosulphate (see previous determination), corrected, if necessary, to 10 c.c. of liquor, is an approximate measure of the sulphide content.

$$\text{Sulphide as H}_2\text{S, g. per 100 c.c.} = \frac{0.17 \times \text{c.c. N/10 I}_2}{\text{c.c. liquor taken}}$$

Spent Liquor.—Sulphide is absent.

Thiocyanate

Ammoniacal Liquor.—The sulphide is first removed from 25 or 50 c.c. of the liquor as in the thiosulphate determination and the liquor is then treated as in the method for spent liquor described below.

Spent Liquor.—25 or 50 c.c. of the liquor "are slightly acidified with sulphuric acid, warmed to about 40° C., a few drops of a saturated solution of iron alum added to clarify the liquor and remove any ferrocyanide that may be present as prussian blue, and the solution filtered through paper pulp with the aid of a Bunsen pump. The thiocyanate in the filtrate is determined as follows:

"To the blood red filtrate (green if polyhydric phenols are

present in quantity) a moderate excess of acid sodium sulphite" or potassium metabisulphite "is added, say, 10 drops of a concentrated solution, and the mixture heated to about 60° C. to effect the reduction of the ferric salt. A distinct excess of a 10 per cent. solution of copper sulphate is then added and the heating continued to incipient boiling. After standing 5 to 10 minutes with occasional agitation, the solution is filtered and the precipitate well washed with hot water until the washings remain colourless on the addition of a drop of ferrocyanide solution. The paper is then pierced and the residue washed back into the flask and 25 c.c. (or less) of a 4 per cent. solution of caustic soda (free from chloride) run into the flask over the paper; the liquor is warmed to about 50° C. to decompose the cuprous salt and a few drops of iron alum added to promote coagulation; it is then filtered through paper pulp, acidified with 5 c.c. of 50 per cent. nitric acid and titrated with N/10 AgNO₃". Iron alum is employed as indicator, preferably as an external one where the original liquor contained large quantities of higher tar acids.

$$\text{Thiocyanate, as CNS, in g. per 100 c.c.} = \frac{0.58 \times \text{c.c. N/10 AgNO}_3}{\text{c.c. liquor taken}}$$

Carbon Dioxide

Ammoniacal Liquor.—"10 c.c. of liquor (more if dilute) are diluted to 400 c.c. in a suitable flask provided with a Bunsen rubber valve; 10 c.c. of ammoniacal calcium chloride (1 c.c. = 0.044 g. CO₂) are added and the whole heated for two hours in a water bath at 100° C." The mixture is filtered hot, preferably through a filter paper which easily goes to a pulp with hot water, and washed free from ammonia with hot water. The filter paper and its contents are then transferred to a flask containing excess (*e.g.*, 25 c.c.) of N/2 H₂SO₄. The mixture is heated to the boiling point with agitation, cooled and titrated with N/2 NaOH.

$$\text{Carbon dioxide, as CO}_2, \text{ in g. per 100 c.c.} = \frac{1.1 \times \text{c.c. N/2 acid}}{\text{c.c. liquor taken}}$$

Spent Liquor.—Carbon dioxide is absent.

Chloride

Ammoniacal Liquor.—10 c.c. of liquor, added to 200 c.c. of distilled water, are boiled free from sulphide and most of the free ammonia and treated as in the method for spent liquor here described.

Spent Liquor.—"10 c.c. are diluted to 150 c.c., 25 c.c. hydrogen peroxide (10 vols. 'free from chloride') added and the whole boiled for 15 minutes to oxidize the thiocyanate, etc.; a further 10 c.c. of peroxide are then added and boiling continued for a further 5 minutes. To the hot solution are added 5 to 6 drops of a 10 per cent. solution of potassium chromate, and the boiling continued for two minutes, then a

few drops of sodium carbonate, with further boiling for one minute. The solution, which should possess a yellow colour, is filtered, cooled and made up to 250 c.c.; an aliquot portion is then titrated with N/10 AgNO_3 (potassium chromate indicator) after neutralizing with dilute nitric acid". This neutralization is very important and it may be necessary to test with litmus paper during the titration itself in order to ensure that neutrality has not been disturbed.

"It is desirable, after oxidation with the peroxide and before the addition of the chromate, to test a drop of the solution with iron alum acidified with nitric acid to ensure that all the thiocyanate has been oxidized. Should oxidation be incomplete, or should the organic matter in solution resist oxidation, further addition of peroxide and potassium chromate must be made and the boiling continued as before".

A blank experiment is made with the same volume of water, peroxide and chromate as in the actual analysis to determine the correction for traces of chloride in the reagents used.

$$\text{Chloride, as HCl, in g. per 100 c.c.} = \frac{0.364 \times 250 \times \text{c.c. N/10 AgNO}_3}{\text{c.c. liquor taken} \times \text{c.c. taken for titration}}$$

Phenols (Monohydric Phenols)

Ammoniacal Liquor.—"To 50 c.c. of liquor are added a few drops of a concentrated solution of ammonium polysulphide to convert any cyanide present into thiocyanate (omit treatment if absent). Avoid using a large excess of polysulphide, as ammonium salts thus introduced tend to reduce the effective soda added to safeguard volatilization of phenol on the water bath. After standing 10 to 15 minutes the sulphide is precipitated by shaking the solution with excess of lead carbonate, and the lead sulphide produced, together with excess lead carbonate, is removed by filtration through paper pulp with the aid of a filter pump". The filtrate is then treated as in the method for spent liquor described below.

Spent Liquor.—"50 c.c. of liquor are evaporated on the water bath with 25 c.c. of a 50 per cent. solution of caustic soda until the salts begin to crystallize. The residual liquid and salts are washed into a distilling flask and rendered slightly acid with 30 per cent. sulphuric acid, a pinch of lead carbonate is added, followed by addition of 1.5 to 2 g. of precipitated chalk; the whole is then well mixed, 25 g. of salt added and 250 c.c. (approximately) of the solution distilled off through a Liebig's condenser". It is convenient to effect the above acidification in the presence of blue litmus paper, addition of acid being discontinued as soon as the paper turns red; the mixture should be cooled during this process. The chalk is added until effervescence ceases and the litmus paper should be blue during the distillation.

The distillate is made up to 500 c.c. and 50 c.c. portions are taken for titration. For a preliminary titration, this quantity is placed in a thin-bottomed stoppered bottle and 2.0 c.c. of N/2 caustic soda added. The contents of the bottle are now heated to 60° C. and 10 c.c., or more, of N/10 iodine solution added. After allowing the mixture to cool naturally, it is acidified with sulphuric acid and titrated with N/10 sodium thiosulphate, with starch as indicator. At the end point the solution changes in colour from blue to salmon pink or a similar tint. If the change is to white, insufficient NaOH was used and the titration should be repeated. If the volume of thiosulphate solution required is less than 5 c.c. the process must be repeated, using a larger volume of iodine. The number of c.c. of iodine consumed in this titration is multiplied by 0.133 and a volume of N/2 caustic soda equal to the product is added to a further 50 c.c. of solution. The procedure is repeated until at least two successive titrations give the same results, the volume of NaOH required being calculated on each occasion.

$$\begin{aligned} &\text{Monohydric phenols, as } C_6H_5OH, \text{ in g. per 100 c.c.} \\ &= \frac{0.1567 \times 50 \times \text{c.c. iodine required}}{\text{c.c. liquor taken} \times \text{c.c. taken for titration}} \end{aligned}$$

Higher Tar Acids

Ammoniacal Liquor.—50 c.c. of liquor are boiled until free from sulphide, rendered just acid with sulphuric acid and made up to the original volume. 15 c.c., or less, are then treated as is spent liquor in the method described below.

Spent Liquor.—A Bunte burette, calibrated from -10 c.c. to 100 c.c. is required, and the free space below the -10 c.c. mark, including the tubulus, must be determined. 15 c.c. (or a smaller volume, if the higher tar acid content is high) of liquor are drawn into the burette followed by 6 c.c. of 10 per cent. caustic soda solution, care being taken that the liquids do not mix. The burette is now placed in a tall cylinder filled with water at air temperature to a height equal to that of the upper stop cock of the burette. "As soon as temperature conditions are constant this stop cock is closed and about 1 c.c. of distilled water run into the cup; the stop cock is then opened and water allowed to enter the burette until pressure conditions are constant". The position of the liquid in the burette is now noted.

"The contents of the burette are shaken for 5 minutes and the burette returned to the water cylinder and pressure conditions adjusted as before by the admission of water. The shaking is repeated for a further 5 minutes and readjustment of pressure conditions again established. If the volume of water then required to restore the pressure does not exceed about 0.2 to 0.3 c.c. the absorption is taken to be complete, otherwise the shaking is repeated".

"The brown alkaline liquid is finally displaced by water in the usual way" and the level of the liquid read at the same pressure and temperature as before. The difference between the initial and final readings gives the volume of oxygen absorbed.

It occasionally happens that, during the shaking process, a good deal of foam is produced which does not disappear when the liquor is replaced by water. With care this may be removed as follows:

After the liquor has been replaced by water the lower tap of the burette is opened to reduce the pressure in the interior and then closed. A small quantity of alcohol is then placed in the cup above the top stop cock and about 1 c.c. is admitted to the burette by opening and then quickly closing the stop cock. The burette is then shaken and the alcohol dissipates the foam. Owing to the high vapour pressure of alcohol, there is now an excess pressure in the burette, and this is released by opening the bottom tap. The solution is again replaced by water and the liquid level read after pressure conditions have been re-established.

Higher tar acids, as parts of O_2 absorbed per 100,000 in aeration test

$$= \frac{1.43 \times 100 \times 273 \times \text{c.c. } O_2 \text{ absorbed} \times \text{mm. barometric pressure} - \text{vapour pressure of } H_2O}{\text{c.c. liquor taken} \times 760 \times \text{absolute temperature}}$$

Oxygen Absorption ($KMnO_4$, 4 hr. 27° C.)

Ammoniacal and Spent Liquors.—100 c.c. of distilled water, 20 c.c. of 25 per cent. sulphuric acid and 50 c.c. of N/80 potassium permanganate are placed in each of two stoppered bottles. 5 c.c. of liquor are diluted to 100 c.c. with distilled water and 5 c.c. of the diluted liquor are introduced slowly with agitation into one of the bottles. The two bottles are then placed in a water bath at 27° C. (80° F.) and allowed to remain there for 4 hours with occasional agitation. A few drops of 10 per cent. potassium iodide solution are now added and the liberated iodine is titrated against N/80 sodium thiosulphate. The difference between the two titrations represents the volume of permanganate consumed by the liquor. The sodium thiosulphate solution keeps better if a pinch of sodium carbonate is added but, even then, it is necessary for the permanganate equivalent of the solution to be determined at frequent intervals. The end point of the titration is determined with the help of starch solution which should not be added until the yellow colour of the iodine is almost discharged. With the above quantities of liquor the oxygen absorbed as parts per 100,000 of liquor is equal to $40 \times$ c.c. of N/80 permanganate consumed by the liquor.

The oxygen absorptions, in parts per 100,000, due to the

different constituents of gas works liquors may be calculated from the following formulæ:

O/A due to Sulphide	= H_2S	in g. per 100 c.c. $\times 1,345$
" " " Phenols	= C_6H_5OH	in g. per 100 c.c. $\times 1,780$
" " " Thiocyanate	= CNS	in g. per 100 c.c. $\times 827$
" " " Thiosulphate	= S	in g. per 100 c.c. $\times 856$

When the O/A due to these constituents is subtracted from the total determined O/A, that remaining unaccounted for is expressed as a "difference" figure. This is due largely to higher tar acids, partly, no doubt, to other substances and possibly to the factor taken for phenols (1,780) not being accurate for all liquors

APPENDIX 2

METHODS OF ANALYSIS OF CONCENTRATED
GAS LIQUOR

The important constituents of concentrated gas liquor are ammonia, carbon dioxide, hydrogen sulphide and phenols. These may be determined in the same way as for ammoniacal liquor, the ammonia being regarded as free ammonia, but it is usually desirable first to prepare a diluted solution of the concentrated liquor. In doing this, great care should be taken to avoid loss of ammonia. One quick and convenient way of doing this is as follows:

A pipette calibrated to contain and not to deliver is used. After washing out a few times with the liquor under test, the pipette is filled with the liquor by blowing liquor into it, not by sucking. The contents of the pipette are then run into a graduated flask containing some water, and the pipette washed several times with water, the washings also being allowed to flow into the flask, which is then made up to the mark and shaken.

Ammonia.—Distillation is not usually necessary. An aliquot portion of the liquor is added to excess standard acid and the solution preferably heated and cooled before the excess acid is determined with standard alkali.

Carbon Dioxide.—The method described on p. 132 may be used. For approximate determination to indicate the liability of the liquor to crystallize, the CO_2 content may be calculated from the following formula:⁸⁶

$$\text{Density} = 1 - 0.0040 \text{ NH}_3 + 0.0094 \text{ CO}_2 + 0.0050 \text{ H}_2\text{S}.$$

The concentrations are in g. per 100 c.c. and the density is that at 15° C. compared with water at 15° C. The ammonia content and density of a liquor are usually determined and the use of the formula is therefore convenient. The term involving sulphide is usually small and only occasional determinations of this constituent are necessary.

Phenols.—The method described on p. 133 may be used.

Sulphide.—If this is to be determined, the diluted solution of the concentrated liquor should be made with water freed from oxygen and the determination made immediately after dilution (p. 131).

APPENDIX 3

METHODS OF EXAMINATION OF SEWAGE

Estimation of the Proportion of Gas Works Liquor in Sewage

It is sometimes desired to know whether a particular sample of sewage contains gas liquor and, if so, in what proportion. This cannot be determined in the absence of a sample of the gas liquor concerned but, when this is available, a very fair estimate of the proportion may be made by the use of a colorimetric method based on the reaction between thiocyanate and acidified iron alum. For approximate results, the following procedure may be adopted:

The sewage under examination is freed, as far as possible, from suspended matter by settling, filtration or centrifuging, and introduced into a 100 c.c. Nessler cylinder up to the mark. Quantities, *e.g.*, 5, 10, 20, 30 c.c., etc., of a 2 per cent. solution of the gas liquor in distilled water are introduced into other Nessler cylinders, which are also made up to the mark with water. Each c.c. of the diluted liquor used is equivalent to 0.02 per cent. of liquor in the final mixture. To all the Nessler cylinders are now added 1 c.c. of strong nitric acid. This usually discharges any colour in the sewage and any produced by oxidation in the liquor mixtures. 1 c.c. of an iron alum solution is then added to each cylinder, which is then shaken. The red colorations produced in the solutions are immediately compared. The concentration of gas liquor in the sewage is approximately equal to that in the liquor water mixture which produces the same intensity of colour. The method gives results sufficiently accurate for most purposes.

ANALYSIS OF SEWAGE AND PURIFIED SEWAGE

It is not proposed to give details of the methods of analysis of sewage and purified sewage; they may be found in "Methods of Chemical Analysis as applied to Sewage and Sewage Effluents", drawn up by the Ministry of Health and published by H.M. Stationery Office, 1929. In view, however, of the frequency with which reference has been made to the oxygen absorption (O/A) and biochemical oxygen demand (B.O.D.) tests and of the significance which may be attached to them, the following brief descriptions of the tests are given:

Oxygen Absorption

The reagents required for the determination are N/80 potassium permanganate (0.394 g. KMnO_4 per litre), N/80 sodium thiosulphate and 25 per cent. sulphuric acid. Into each of two stoppered bottles are placed 10 c.c. of the dilute acid and 50 c.c. of the standard permanganate solution. To the contents of one bottle are added 10 c.c. of sewage or 100

c.c. of purified sewage (intermediate quantities may be used if the sewage is very weak or the effluent is unsatisfactory). The volume of liquid in each bottle is now made up to 160 c.c. with distilled water and the bottles are kept at 27° C. for 4 hours with occasional rotation. At the end of this period, a few drops of potassium iodide solution are added and the liberated iodine is titrated against the sodium thiosulphate solution, starch, added just before the end point, being used as the indicator. The difference in titration between the two bottles represents the amount of permanganate consumed by the sewage or effluent, and quantities should be so arranged that not more than about half of the added permanganate is so consumed. The oxygen absorption in parts per 100,000 is given by

$$\frac{10 \times \text{c.c. permanganate consumed}}{\text{c.c. sewage or effluent taken}}$$

It must be borne in mind that the test is empirical and that complete reaction with permanganate does not take place in the four hours. It is therefore essential that the conditions of the test should be accurately reproduced in all determinations.

Biochemical Oxygen Demand

This test requires care and practice and should not be attempted unless it is intended to carry out determinations regularly over a considerable period. In all cases, it is desirable that duplicate determinations should be made.

Two glass stoppered bottles of 300 to 400 c.c. capacity are thoroughly cleaned. A suitable mixture of sewage or sewage effluent and tap water is prepared, say, 10 c.c. of sewage or 200 c.c. of effluent to 1 litre. The tap water should have been stored in a stoppered bottle in the laboratory for several days. Both reaction bottles are now completely filled with the diluted sewage and stoppered, all air bubbles being carefully excluded. The dissolved oxygen in one of the bottles is immediately determined as follows:

The stopper is removed and 0.9 c.c. of concentrated sulphuric acid introduced, followed by 1 c.c. of N/8 potassium permanganate. The latter should be admitted well below the surface of the liquid. The bottle is again stoppered, the excess of liquid being displaced as the stopper is inserted, and, after shaking, is allowed to stand for 20 minutes. If the colour of the permanganate is discharged during this time, a further quantity must be added. After 20 minutes, 1 c.c. of 2 per cent. potassium oxalate solution is added in the same way, the bottle is again shaken and left until the permanganate colour disappears. When this has occurred, the stopper is again removed and 1 c.c. of a 33 per cent. manganous chloride solution is added from a pipette, the outside of which must be wiped before the tip is inserted into the bottle. The solution should be admitted below the surface of the liquid

but not at the bottom of the bottle. An immediate addition is then made of 4 c.c. of a mixed solution containing 70 per cent. KOH and 10 per cent. KI. The bottle is again closed and shaken. A further shaking, after a few minutes, assists in the settlement of the manganese hydroxides. When this has occurred, at least 5 c.c. of concentrated hydrochloric acid are run into the bottle, which is stoppered, reshaken and allowed to stand out of strong light for 5 minutes. The bottle is again shaken and 50 c.c. removed for titration with N/10 thiosulphate, using starch as indicator. As the volume of thiosulphate required will not exceed 4 to 5 c.c., a small burette accurately graduated to 0.05 c.c. should be used and the end point determined to 0.01 or 0.02 c.c.

The second bottle, containing the diluted sewage, is kept tightly stoppered at 18° C. for 5 days and the residual dissolved oxygen is determined in the same way. The difference between the titration figures of the initial and final bottles is a measure of the dissolved oxygen used during the 5 days' incubation period. In parts per 100,000 of the original sewage or effluent this is given by

$$\frac{10 \times \text{c.c. titration difference} \times \text{c.c. tap water and sewage in diluted sewage}}{\text{c.c. solution taken for titration} \times \text{c.c. sewage in diluted sewage}}$$

During the determination, a certain amount of sewage is lost due to the fact that each time a reagent is added an equal volume of liquid is displaced, but the errors thus introduced are negligible in relation to the accuracy of the method. If the properties of the liquid under test are unknown, it is advisable to carry out the determination with a number of dilutions with tap water, in order that at least one will give a reasonable titration difference and yet not consume all the oxygen.

APPENDIX 4

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